STUDY OF FLUOROAPATITE REACTIONS

THE EFFECT OF METAPHOSPHATE MELTS ON FLUORINE-CONTAINING SUBSTANCES

By

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INTRODUCTION

The Occurrence and Use of Apatites

One of man's most useful minerals is phosphate rock. Its major use as the source for phosphate fertilizers is well known. Phosphate rock is primarily composed of a group of minerals called apatites, the most typical representative of which is fluoroapatite[1] with the formula $Ca_{10}F_2(PO_4)_6$. Natural apatites vary greatly not only in kind and variety of impurities present, but also in the composition of the apatite itself. This is true even for two mineral samples from the same deposit.

The phosphate rock deposits of varying composition can be found in many places throughout the world. The North American continent, however, is particularly rich in this mineral, which in this case consists essentially of submicrocrystalline fluoroapatite containing some excess of fluorine (27), and is usually found in an admixture of iron, aluminum, and silica compounds.

The structure of crystalline apatites has been studied, and it has proved to be remarkably stable, permitting a variety of unusual types of substitutions involving a considerable number of ions. The most important of these changes occur where the fluoride ion in fluoroapatite is

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[1]In this work the prefix "fluoro-" is applied in the term "fluoroapatite" in conformity with the general usage of this prefix to designate compounds containing fluorine (e.g., fluoroaluminates). The Tennessee Valley Authority investigators use "fluorapatite", and some

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substituted partly or fully by hydroxyl, chlorine or carbonate groups, forming the respective apatites. The occurrence of extensive series of solid solutions among these apatite type structures are also very common.

The apatites are readily formed in solid state reactions as well as in aqueous solutions, in which they are quite stable. For example, a suspension of hydrated tricalcium phosphate may be used to induce the formation of fluoroapatite by the precipitation of solute fluoride ions, thus effecting complete removal of fluorides from ground waters (49).

Ever since the phosphate fertilizer industry existed, numerous investigators have been seeking better industrial procedures for processing phosphate rock, but in recent decades more attention is being paid to these materials as chemical systems. Basic studies have been started, and are being carried out by several independent groups, each interested in their own particular applications. Considering the complexity of phosphate systems, the research done until now has been only a modest beginning in disentangling the variety of problems related to these materials.

In this country the Tennessee Valley Authority has done extensive and excellent work in the field of phosphates in developing new industrial procedures as well as conducting basic studies of the phosphatic compounds. The major purpose of their work has been the increase of the phosphorus availability in the processed materials. The results of their findings have been made public in a series of reports and articles (18b, 68).

The study of the structure of apatites has deserved considerable

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other authors prefer "fluor-apatite" or "fluoro-apatite".

attention on the part of medical people and crystallographers particularly since the discovery that the mineral constituent of bone and of the enamel and dentine of teeth is essentially hydroxyapatite, as established by X-ray crystal analysis (4).

In recent years a number of new practical applications have been found for synthetical apatite type materials. For example, the alkaline earth halophosphates possess very favorable characteristics as fluorescent materials, and are already in wide-spread use in fluorescent lamps in England (55).

The Fluorine Problem

In the near future wide attention will be directed to the fact that the North-American phosphate rock constitutes a practically inexhaustible source for fluorine-containing compounds. Presently this element is won from fluorspar (CaF_2), but since the domestic resources of this mineral in highgrade purity are being rapidly depleted, it has been placed on the list of critical materials by the Strategic Materials Committee of the U. S. Government (21), and recommended for stockpiling.

At this time no efficient and economical industrial process is known for the extraction of fluorine from phosphate rock.

The fertilizer industry has long been concerned about this problem for its own reasons, since the presence of fluoride exerts a deleterious effect on the availability of phosphorus in the soil and acts as a poison if fluorine-containing phosphates are used as cattle-feed supplement.

The known and practiced methods for the extraction of fluorine-containing components from phosphate rock are:

1. dissolution of the mineral in strong aqueous acids, and the
precipitation of fluorine as fluoride, or silicofluoride (18b);

2. treatment of phosphate rock with sulfuric acid and heating (23);

3. defluorination of the mineral at high temperatures, above
1300°C., in the presence of silica and water vapor (17, 67).

Part of the extracted fluorine, in the form of hydrogen fluoride
and silicon tetrafluoride, can be recovered from the flue gases by the
adsorption of hydrogen fluoride in (18a) lime-packed towers, and by
scrubbing silicon tetrafluoride with alkaline solution (52). In the
latter case fluorosilicates will be formed.

The above-mentioned procedures have been used only to a minor
extent, and it is improbable that any of them could be adopted to a
wide-scale economic industrial process for the purpose of fluorine
extraction.

The Objectives of Further Studies

More knowledge about the apatite systems is necessary for the
development of new approaches which would enable more efficient bene-
ficiation of all the materials present in phosphate rock. This can be
accomplished only by thorough fundamental studies, which should be
extended to a large number of phosphate systems under a variety of
conditions.

Almost all previous work has been done on natural minerals, and
although much of a general nature has been published very little precise
scientific knowledge is available on phosphate rock. A reproducible
fluoroapatite has only been prepared within the past several years and

the rates of reactions of this pure material with other chemicals have not yet been studied.

The contribution of a small group of investigators must of necessity remain rather limited considering the demands of the field. It was, however, hoped that this work would help to emphasize the need to look at the problem as a whole, and add to the basic knowledge concerning these important materials.

The general objective was set to initiate a broad program of study of apatites and other related materials for the purpose of finding new basic facts about the physical properties of well defined phosphatic systems, their reactivities and rates of reactions. The coordination of the available information from various sources would form a part of this task.

This dissertation summarizes parts of the work which was carried out with the purpose of studying the possibilities of novel fluoroapatite reactions below 1000°C. with special attention to the behavior of fluorine. One of the favorable decomposition reactions was then selected for a closer study.

Furthermore, there was the preliminary task of choosing a feasible method for the production of chemically pure fluoroapatite, and the comparison of suitable analysis methods for these materials.

The subject matter in this dissertation is composed of three independent parts.

In the following three chapters the synthesis, the analysis and the crystallographic properties of fluoroapatite are described.

The chapters in the middle section discuss the general possibilities

of fluoroapatite reactions with chemicals in various phases. The refer-
ences to the known reactions have been included, and the results of a
variety of experiments carried out in this laboratory have been
presented. The standard free energy changes were calculated for a
number of reactions and the results have been given.

The third and major part of the dissertation describes and dis-
cusses the interaction of metaphosphate melts with fluorine-containing
substances. The experimental procedures for the study of the special
reactions were developed in this laboratory.

SYNTHESIS OF FLUOROAPATITE

Synthesis Methods

Tricalcium phosphate combines readily with pulverulent calcium fluoride forming mixtures which register characteristic properties of fluoroapatite. Numerous investigators have observed this reaction under various conditions.

The process may take place in aqueous solutions, although in this case the precipitate is always contaminated with other phosphates (6).

Stoichiometric amounts of tricalcium phosphate and calcium fluoride, intimately mixed, produce fluoroapatite after gradual heating of the mixture (5) to $950°C$.

Fluoroapatite has been prepared by the reaction of hydroxyapatite with calcium fluoride in the solid state (8) above $600°C$.

Wallaeys has synthesized mixed fluoro-, chloro-, and hydroxyapatites. The structure and isomorphism of these compounds are described (70, 71).

The phase diagram of the system calcium fluoride - tricalcium phosphate has been studied by R. Nacken. According to him fluoroapatite will be formed in a molten mixture of calcium fluoride with an excess of tricalcium phosphate (50, 54).

In the foregoing preparations the identity of fluoroapatite was usually established by X-ray analysis, and little was mentioned about the chemical purity of the products or the presence of other phases. In

this respect the latest and the most reliable procedure has been given

by the TVA scientists under the direction of Kelly L. Elmore, Chief of

Research Branch, Division of Chemical Development. It was decided to

adopt their method for the synthesis of fluoroapatite, hydroxyapatite,

and tricalcium phosphate as described by Dr. K. L. Elmore (14).

Recommendations of the TVA Group

The following directions are an excerpt from a personal letter by

Dr. K. L. Elmore, April 1, 1953.

Prepare a stock of raw materials as follows:

Calcium Carbonate: Recrystallize reagent-grade calcium nitrate
and precipitate calcium carbonate with ammonium carbonate.
Calcium Fluoride: Distill reagent-grade hydrofluoric acid in
a platinum still and precipitate calcium fluoride with precipitated
calcium carbonate.
Calcium Metaphosphate: Recrystallize reagent-grade monocalcium
phosphate monohydrate. Heat the monocalcium phosphate carefully
to 600°C. in a platinum boat to form crystalline calcium
metaphosphate.
Tricalcium Phosphate: Mix calcium metaphosphate and calcium
carbonate in stoichiometric proportions to form tricalcium
phosphate. Heat the mixture in a platinum boat at 1150°C. for
five hours. It may be necessary to make adjustments in composition.
Hydroxyapatite: Precipitate a composition approximating
hydroxyapatite by the method of Rathje (57). Dry the precipitate
at 105°C. and then heat in a platinum boat at 950°C. in an
atmosphere of 20 per cent steam and 80 per cent nitrogen for at
least 72 hours to promote crystal growth.
Fluoroapatite: Prepare a stoichiometric mixture of tricalcium
phosphate and calcium fluoride. Heat the mixture in a platinum
boat at 1350°C. for at least 30 minutes in a stream of dry
nitrogen. Again, adjustments of composition may be necessary.

Complete reaction requires grinding and intimate mixing. The
resulting products have small crystal size. In a separate
publication (13) the conditions are described by which large,
well defined crystals of fluoroapatite can be produced from
sodium fluoride flux in a vacuum furnace heated by induction.
Difficulties were encountered in keeping the crystals completely
free of flux. In none of the preparations was it advisable to
prepare more than fifty grams in one batch.

The first task of the present study was to prepare various samples of fine crystalline fluoroapatite according to the TVA recommendations. The directions given above are quite generally worded, and it was found that an extensive review of the literature on the subject along with actual experiments had to be carried out in order to determine the influencing factors in the preparation of the materials needed.

The procedure for fluoroapatite synthesis can be divided into seven separate steps:

1. Recrystallization of monocalcium phosphate monohydrate.
2. Conversion of monocalcium phosphate monohydrate into metaphosphate.
3. Recrystallization of calcium nitrate tetrahydrate.
4. Distillation of ammonium carbonate and precipitation of calcium carbonate.
5. Ignition for formation of tricalcium phosphate.
6. Precipitation of calcium fluoride.
7. Ignition for formation of fluoroapatite.

In the following section some of the essential details of each step will be pointed out along with major references for background information.

Synthesis of Chemically Pure Fluoroapatite

Recrystallization of Monocalcium Phosphate Monohydrate.-The monocalcium phosphate obtainable on the market usually contains free phosphoric acid, sometimes up to 5 per cent, although the salt may appear quite dry. If the commercial material contains only monocalcium

phosphate as a solid phase, a satisfactory acid-free product can be obtained by washing out the free acid with a suitable organic solvent. Frequently, however, the C.P. salt carries a small quantity of dicalcium phosphate, which can be removed only by recrystallization from a solution of the proper composition (9).

Monocalcium phosphate monohydrate, Fisher Certified Reagent, was used in this laboratory, and recrystallized according to the directions of W. L. Hill and S. B. Hendricks (32).

It is difficult to remove every trace of excess phosphoric acid from the crystals. Washing with alcohol and ether has been used for removing (64) the excess acid, but acetone (31, 60) is to be preferred. Acetone was dried over anhydrous potassium carbonate and filtered before use.

Conversion of Monocalcium Phosphate Monohydrate into Metaphosphate.-Heating of monocalcium phosphate produces varying results, depending upon whether charges are heated directly or in a step-wise fashion to the selected temperature. Step-wise heating gives somewhat more reproducible results, particularly when hydrated monocalcium phosphate is used as a starting material. This salt, when it is heated rapidly, melts incongruently near $150^{\circ}C.$, and the accompanying rapid loss of water vapor causes frothing; frequently with loss of material from the container, and formation of a tough mass. Fusion can be avoided (33) by first heating the charge at $125^{\circ}C.$ to expel water of crystallization, but further heating in the range 200° to $600^{\circ}C.$ yields an unpredictable mixture of phases consisting of glasslike amorphous material, and one or more of at least three crystalline phases. This

mixture, however, can be converted to stable β-calcium metaphosphate by heating between 600° and 700°C.

In this laboratory, about a fifty gram lot of pure, acid-free monocalcium phosphate monohydrate was heated, first at 125°C. for two hours to expel water of crystallization, and then at 400°C. for two hours; after reheating between 600° and 700°C., the substance was cooled in air. The product obtained by this method (34) had a sandy crystalline appearance and could be easily pulverized.

Recrystallization of Calcium Nitrate Tetrahydrate.-Calcium nitrate, Mallinckrodt Analytical Reagent, contains as major impurity a total of 0.20 per cent of magnesium and alkali salts. Richards and Hönigschmid proved (50) that such impurities can be removed by the re-crystallization of the nitrate.

Calcium nitrate is a deliquescent and very soluble salt with a great tendency to form supersaturated solutions. Owing to the ready solubility of calcium nitrate in organic solvents, the crystals could not be freed from solution by washing with alcohol, acetone, pyridine, etc. (3).

In this laboratory, about 200 grams of calcium nitrate tetra-hydrate were dissolved in 25 ml. of water in a platinum dish and heated to about 100°C. The solution was cooled overnight in a refrigerator and seeded with a small crystal of calcium nitrate tetrahydrate. The crystal formation progressed very rapidly in cool solutions. Suction on a fritted-glass funnel was applied to separate the mother liquor from the crystals.

Distillation of Ammonium Carbonate and Precipitation of

Calcium Carbonate.-Pure ammonium carbonate, Mallinckrodt Analytical

Reagent, was distilled in a glass apparatus and condensed in a flask

with ice-cold water. The fresh ammonium carbonate solution was added

to the calcium nitrate solution, and the precipitated calcium carbonate

was filtered and washed with plenty of distilled water. The product

was preserved in a platinum dish in which it was first heated to 105°C.

for a couple of hours and then at 400°C. for a short time.

Ignition for Formation of Tricalcium Phosphate.-Calcium meta-

phosphate and calcium carbonate were mixed in stoichiometric proportions

and heated in a platinum shell at 1150°C. for five hours. There was

always some loss of phosphorus during the ignition, thus the Ca/P ratio

in the product was usually somewhat higher than the theoretical value.

The ratio can be corrected by an addition of a right amount of

calcium metaphosphate to the product and by the repetition of furnace

treatment.

The necessary quantity of calcium metaphosphate can be calculated

from the following equation:

$$\frac{W(Ca) + r(Ca) \ X}{W(P) + r(P) \ X} = 1.9406$$

W(Ca) - weight of calcium in the sample by analysis

W(P) - weight of phosphorus in the sample by analysis

r(Ca) - ratio of $Ca/Ca(PO_3)_2$ = 0.20238

r(P) - ratio of $P_2/Ca(PO_3)_2$ = 0.31290

X - amount of calcium metaphosphate necessary

After rearrangement and insertion of the numerical values the formula has this expression:

$$\frac{W(Ca) - 1.9406\ W(P)}{0.40478} = X$$

For example, in one case 0.060 gr. of calcium metaphosphate had to be added to five grams of tricalcium metaphosphate to obtain the correct Ca/P ratio which is 1.9406.

Precipitation of Calcium Fluoride.-Crystalline calcium fluoride was produced by adding a slight stoichiometric excess of hydrogen fluoride in aqueous solution to a suspension of precipitated calcium carbonate. Weighings and other operations were carried out in platinum dishes. The product was washed with abundant water, dried at 110°C. for several hours, and then heated to about 700°C. until the weight remained constant.

At higher temperatures, calcium fluoride volatilizes in noticeable quantities. Thus the loss in grams per sq. cm. of surface for 24 hours of calcium fluoride heated in air has been reported (2) to be 6.3 mg. at 1250°C. and 23.5 mg. at 1400°C.

Ignition for Formation of Fluoroapatite.-The heating unit in use was a Burrell High Temperature Electric Furnace, Model L-C-M, maximum temperature 1400°C.

Stoichiometric mixtures of tricalcium phosphate and calcium fluoride were heated in a platinum shell for about an hour at 1350°C. The charge was covered by another platinum shell which in its inverted position rested with the edge on the even floor of the furnace, whereas its bottom touched the upper edge of the first shell. Thus, there was formed a doubly isolated space with hindered diffusion between the space

above the charge and the furnace atmosphere. The first shell with the charge was adjusted a little above the floor of the furnace, supported by pieces of firebrick, and underneath it was a platinum cover with calcium fluoride in order to provide a vapor phase of the salt at high temperatures. The heating proceeded gradually in the course of about ten hours. Nitrogen, dried by the passage through a long tube of silica gel was led into the furnace during the ignition, primarily for the purpose of keeping the furnace atmosphere as dry as possible.

The results of various samples indicated that some fluorine-containing compound had been volatilized during the treatment, and that usually the phosphorus content was also lowered as compared with the initial composition.

Three mixtures were then prepared containing an excess of calcium fluoride - 105, 110, and 115 per cent respectively, as compared with the stoichiometric requirement. The following table presents the compositions of the three preparations.

TABLE 1

COMPOSITION OF PURE FLUOROAPATITE SAMPLES

Sample	Percentage by Weight of the Component Elements		
	Calcium ± 0.10	Phosphorus ± 0.10	Fluorine ± 0.08
105% CaF_2	39.94	18.32	3.56
110% CaF_2	40.05	18.20	3.74
115% CaF_2	40.25	18.18	3.96
Theoretical	39.735	18.428	3.767

By adding ten per cent excess calcium fluoride, the Ca/P ratio
has to be newly adjusted by a proper amount of calcium metaphosphate.
This quantity can be calculated from a formula expressing the Ca/P ratio
in fluoroapatite.

The initial formula is quite long; after the substitution of
numerical values and contraction it is:

$$0.0090866 \ W(Ca-P) = X$$

W(Ca-P) = weight of tricalcium phosphate in grams

X = additional amount of calcium metaphosphate

needed in grams

A Simplified Procedure for Fluoroapatite Synthesis

The procedure described previously for the synthesis of
chemically pure fluoroapatite yields good results, but the preparation
of starting materials is laborious. Need was felt for a simplified
procedure which would facilitate the preparation of fluoroapatite in
sizeable quantities with good quality and acceptable purity.

A new procedure was developed which utilized the commercially
available quality chemicals and dispensed with the recrystallization of
salts.

Materials.-The following materials were used - monocalcium phos-
phate monohydrate, Mallinckrodt's Analytical Reagent, was held in dry
acetone over a period of three months. First, the solvent was changed
every other day; afterwards once a week. Acetone was removed carefully
from the salt by drying at 50°C.

Mallinckrodt's calcium carbonate (300 g.) and Baker's calcium

fluoride (200 g.), both Analytical Reagents, were treated for three months with approximately twenty liters of water, in each case, at room temperature. After the treatment, the salts were dried at 140°C. and calcium fluoride was further ignited at 600°C. for two hours.

Results.-Using these three salts as starting materials, five lots of fluoroapatite were prepared following the standard heating procedures. The appearance and chemical properties of the new products were identical with those of the previous preparations after the first ignition. The lots were designated by letters a-e. The analysis results are presented in the following table.

TABLE 2

COMPOSITION OF FLUOROAPATITE SAMPLES PREPARED
BY THE SIMPLIFIED PROCEDURE

Sample	Ratio Ca/P	Percentage by Weight of the Component Elements		
		Calcium ± 0.10	Phosphorus ± 0.10	Fluorine ± 0.03
a	2.147	39.42	18.36	3.42
b	2.145	39.47	18.41	3.42
c	2.184	39.11	17.50	3.60
d	2.179	39.66	18.20	3.67
e	2.203	39.78	18.06	3.65
Theo-retical	2.1563	39.735	18.428	3.77

<u>Identification of Fluoroapatite.</u>-Microscopic observations rendered positive proof concerning the identity of the products, and gave an indication regarding the uniformity of the materials.

The available instrument was a Bausch & Lomb Petrographic Microscope, Model LC, with accessories.

Fine grains of the material were immersed in various oils of known refractive indices, and the movement of Becke lines was observed. The small crystal size prohibited the determination of the interference figures, but the characteristic birefringence could easily be followed. Weak birefringence persisted uniformly throughout the material.

All preparations exhibited identical crystallographic and optical properties. The mass of the material possessed a refractive index in the range of 1.630 to 1.632, which agrees with the values, $\mu_\alpha = 1.6325$ and $\mu_\gamma = 1.630$, reported by R. Nacken (54) for artificial fluoroapatite.

Minor amounts (a fraction of one per cent) of different crystals were observed, the optical properties of which suggested the presence of some unreacted calcium fluoride and tricalcium phosphate.

The material can be cleaned by treating it first with sodium carbonate solution (2 g. in 100 ml.) at about $70^\circ C$. for several hours, with subsequent standing in a two per cent citric acid solution at room temperature. The total loss of the material is small, and the product has a uniform appearance under the microscope as clean fluoroapatite.

ANALYSIS OF FLUOROAPATITE

The analysis of fluoroapatite constitutes a problem of determining quantitatively phosphorus, calcium, and fluorine in the presence of one another, and practically in the absence of other elements except in the smallest quantities.

A very extensive literature has been accumulated on the subject of the analysis of phosphate rock and phosphatic fertilizers. The described procedures are quite involved because of the necessity of taking account of the numerous interfering elements.

In the case of pure fluoroapatite, one is not concerned with such a multitude of components, and it was hoped that simpler and less time-consuming procedures could be found. For that purpose, the favorable features of various methods were combined and tested on the phosphatic materials. Only volumetric and gravimetric determinations were considered. Due attention was paid to the widely used official or recommended procedures of the Bureau of Standards and of the Association of Official Agricultural Chemists.

Preparation of Analysis Standards

Calcium.-Calcium carbonate, C.P. Reagent, can be used with advantage as a standard substance after washing with ample distilled water and drying at 110°C. to constant weight.

Phosphorus.-Potassium dihydrogen phosphate is being widely used

as a standard substance for preparing solutions of known phosphate con-
centration. Purification beyond the reagent grade can be effected by
recrystallization (37). As a test for the purity of the material, the
loss on ignition should not be less than 13.13 per cent nor more than
13.33 per cent.

Fluorine.-Sodium fluoride, Reagent Grade, dried for one hour at
105°C., offers a satisfactory standard for fluorine determinations.

Calcium Determination

Practically all methods for calcium determination, whether by
volumetric or gravimetric procedures, start with the precipitation of
calcium as calcium oxalate monohydrate. It has been shown experimentally
that calcium ion can be quantitatively precipitated in the presence of
phosphate and fluoride ions (up to about 5% fluorine), and some other
elements as they usually occur in the phosphate rock.

Seven methods of calcium precipitation were recorded, and five
of them (25, 35a, 36b, 46, 72) tested. The procedures differed from
each other in the volume of the sample in the concentrations of the rea-
gents, the indicators used, and the temperature of ammonium oxalate
during the addition.

Volumetric Determination.-Precipitation (41a) followed by titra-
tion according to the description by Kolthoff and Sandell (41b), is a
simple and recommendable procedure. The accuracy is about one per cent
or somewhat better.

The procedure by Lingane (46) is the latest and claims the
highest accuracy, about 0.1 per cent. The method is relatively fast, but

needs more experimental verification.

In determining the proper endpoint of the titration with permanganate, the recommendations of Fowler and Bright (22) should be observed.

Gravimetric Determination.-Under suitable precipitation conditions, calcium can be weighed in the form of calcium oxalate monohydrate dried at room temperature, according to Sandell and Kolthoff (41b). Accuracy is about 0.2 per cent.

Washburn and Shear (72) dried the precipitate at 105°C. and obtained good results as confirmed by the experiments in this laboratory. Accuracy is approximately the same as in the previous case.

The most accurate weighing form for calcium ion is considered to be calcium carbonate. The accuracy amounts to 0.1 per cent or less in the absence of interfering ions (74). The precipitate has to be heated at about 500°C. for one hour.

Calcium sulfate is a good weighing form for calcium (41a) if it can be directly precipitated from the solution free from other earth alkali elements. The ignition temperature does not have to be closely observed (the range is from 105° to 890°C.).

This method was used most frequently in this laboratory with good results which were checked by the carbonate method. Accuracy was about 0.1 per cent.

Phosphorus Determination

In the presence of calcium, two courses are open for the precipitation of phosphorus in the form of orthophosphate.

1) The precipitation of magnesium ammonium phosphate may be

made in the presence of much ammonium citrate, which prevents the pre-
cipitation of calcium and other phosphates.

2) Phosphorus may first be separated from the interfering
elements by precipitation as ammonium phosphomolybdate in acid medium.
This precipitate may then be dissolved in ammonia and magnesium ammonium
phosphate precipitated.

The first method as described by Hoffman and Lundell (36a)
promises to be a more rapid procedure and gives (47) equally accurate
results.

The second method has been in most wide use in many practical
procedures for separating phosphorus from a multitude of interfering
elements. Besides, it is the basis for the ordinary volumetric deter-
mination of phosphorus (1).

Gravimetric Determination.-The most accurate results, within 0.1
per cent of the total phosphate, are obtained by igniting the ammonium
magnesium phosphate at high temperatures to pyrophosphate (35b).

Alternatively, the ammonium magnesium phosphate hexahydrate may
be weighed directly after drying the precipitate at room temperature (19),
or at about $37^{\circ}C$., according to Washburn and Shear (72) who obtained good
accuracy (about 0.2 per cent). This method, however, as employed in
this work was not as reliable as the pyrophosphate procedure, primarily
because of the difficulties in obtaining a reproducible tare weight for
the Pyrex fritted glass crucibles. In the course of ordinary phosphorus
analysis, the fritted glass crucibles lost first up to 1.0 mg. in weight
per determination and later on about 0.1 to 0.5 mg. per determination.
These crucibles were also somewhat hygroscopic and gained in weight up

to one milligram standing in room temperature.

Volumetric Determination.-In the volumetric method the ammonium phosphomolybdate is dissolved in a known amount of standard sodium hydroxide solution, and the excess of the latter is back-titrated with standard acid, phenolphthalein being used as indicator. The accuracy of the volumetric procedure is hardly any better than one per cent. Several attempts have been made to improve the procedure, for example, Kassner (39) claims very good accuracy, about 0.1 per cent, for his method employing mixed indicators.

Fluorine Determination

For the determination of fluorine in phosphatic materials, the most tested and the most widely used method is that outlined by Willard and Winter (75), which has undergone numerous modifications by a host of other investigators. A good summary about the modifications of the Willard and Winter fluorine determination method has been given by Reynolds and Hill (58). The method used in this laboratory corresponded closely to the procedure as given by Willard and Winter and modified by Reynolds and Hill.

THE MOLECULAR STRUCTURE OF FLUOROAPATITE

The unit cell and space group of the crystal lattice of fluoro-
apatite have been determined by the following investigators:
Leonhardt (45), St. Naray-Szabo (63), Mehmel (50), Beevers and
McIntyre (4).

Apatite is a typical example of the crystal class C_{6h}; etching
experiments and Laue photographs confirm this symmetry. The unit cell
contains 42 atoms, ordinarily written in the form $CaF_2.3\ Ca_3(PO_4)_2$.
The unit cell of the apatite structure has two equal edges inclined at
120° to one another. The length of these edges is 9.37 A° in the case
of fluoroapatite. The third edge is at right angles to these and has a
length of 6.88 A°.

The cell possesses vertical symmetry axes of three kinds:
1) passing through the points (two-thirds, one-third) and (one-third,
two-thirds) of the cell are three-fold rotation axes; 2) passing through
the corners of the unit cell are hexagonal screw axes; and 3) passing
through the halfway points of the cell edges and through the center are
two-fold screw axes.

There are also eight centers of symmetry and two mirror planes
parallel to the xy plane.

The atomic[1] surroundings are as follows:

Fluorine   - three Ca at one level

Phosphorus - tetrahedron of four O

Calcium I   - (on three-fold axis) nine O

Calcium II - (on reflection planes) an irregular
                  polyhedron of one F and five O

Oxygen   - tetrahedron of one P and three Ca

While investigating the compositions of some western phosphate
rocks Hendricks, et al. (28), carried out a number of X-ray diffraction
measurements on the group of compounds structurally similar to fluoro-
apatite. The compositions and the crystallographic properties of these
minerals and of some artificial products support the suggestion that the
fluoride ion in fluoroapatite can isomorphously be replaced by carbonate,
sulfate, silicate, or hydroxyl groups; and by oxygen, chlorine, bromine,
or iodine ions.

Furthermore, the crystallographers have provided evidence that
the calcium ion in the lattice can be replaced completely or partly by
the ions of the following elements: Be, Mg, Sr, Ba, Pb, Zn, Ni, Cd, Cu,
Fe, Mn, Al, Mo, or Cr; and the phosphorus ion by V, As, Sb, S, C, Si, or
Al ions.

Fluoroapatite is the stablest of all these substituted structures
both thermally and chemically. The specific feature of the fluoroapatite
structure is the arrangement of calcium and phosphate ions in such a way
that channels exist within the crystal into which the fluorine ions fit

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[1]The elements are present in the form of ions: F^{-1}, O^{-2},
P^{+5}, Ca^{+2}.

with close packing. This fact evidently accounts for the remarkable
stability of fluoroapatite, and makes it the substance to which the
numerous other structurally similar compounds can be compared in their
chemical reactivity and physical properties.

SOLUBILITY OF FLUOROAPATITE IN AQUEOUS SOLUTIONS

General Behavior

Fluoroapatite can be regarded as a basic substance due to its high Ca to P ratio, and therefore it may be expected to react more readily with acidic materials.

In aqueous solutions, the mineral acids decompose fluoroapatite slowly at room temperature, faster at higher temperatures.

TVA is currently carrying out experiments on the solubility of fluoroapatite in various concentrations of phosphoric acid at $25^{o}C$. and $50^{o}C$., including its rate of solution at a pH range between one and four (15).

The solubility of fluoroapatite in solutions of organic acids is rather limited. No reliable data are available yet about such systems.

Alkaline solutions under ordinary conditions do not affect fluoroapatite appreciably.

In respect to the reactions of alkaline solutions with naturally occurring materials, the latest developments are the studies of Japanese investigators (38) concerning the effect of alkali treatment of phosphate rock by extracting fluorine with sodium hydroxide solution under pressure.

Fluoroapatite is very slightly soluble in water. The solubility product, calculated from heat capacity and heat of solution is 3.73×10^{-117} at $25^{o}C$. This value was calculated by the TVA investigators (15).

The Effect of Sodium Carbonate Solutions on Fluoroapatite

In the course of the preparatory work in this laboratory, there was some interest in finding a solution of suitable composition which would dissolve crystalline calcium fluoride in preference to fluoro-apatite. The data on the relative solubilities of these two materials in organic acids are incomplete, and since there was no intention on our part to study the solubility of fluoroapatite in acidic solutions, consideration was given to sodium carbonate solutions. A series of experiments were carried out in order to determine the effect of sodium carbonate solutions on finely powdered fluoroapatite under varied conditions. The results are presented in the following section.

Experimental Results.-The extent of fluoroapatite solubility was followed by phosphate analysis. The materials were treated with sodium carbonate solution and filtered. The phosphate was precipitated in the filtrate with ammonium molybdate. After washing with dilute potassium nitrate solution, the precipitate was titrated with standard sodium hydroxide.

Two grades of fineness of apatite powder a) 250-300 mesh, and b) finer than 300 mesh, were used for the following experiments.

Five grams of each material were let stand for three weeks at room temperature in 100 ml. of water with two grams of sodium carbonate, with occasional stirring. The solid matter was separated from the solution by filtration. The phosphate was precipitated in the filtrate, and the titration gave the following values: a) 1.1 mg. and b) 1.5 mg. phosphorus.

The residue on the filter paper was similarly treated for five more weeks. The respective titration results were: a) 2.7 mg. and b) 2.8 mg. phosphorus.

In the next experiment, the two solutions with 1) 1.0 g. and 2) 0.5 g. of fluoroapatite (250-300 mesh) were boiled with two grams of sodium carbonate in 100 ml. of solution for two hours and filtered at room temperature. The results were: 1) 0.9 mg. and 2) 0.8 mg. phosphorus determined in the filtrates.

Repeating the procedure with the residues after filtration and with new solutions, the following values were found: 1) 0.8 mg. and 2) 0.6 mg. phosphorus.

A higher carbonate concentration increased the phosphate concentration in the solution, and filtering of the solution while hot gave somewhat higher values.

The amount of phosphorus determined in the solution after treatment was in the order of one to two per cent of the total phosphorus present in the fluoroapatite sample (184 mg. in one gram of fluoroapatite).

Conclusions.-The results lead to the conclusion that sodium carbonate solutions affect the solubility of fluoroapatite. The total effect does not exceed two per cent with one treatment at the given concentration of sodium carbonate.

Several factors influenced the rate and extent of the increased solubility of fluoroapatite, but generally there seemed to be an equilibrium value of about two to three milligrams of phosphorus in 100 ml of a solution containing two grams of sodium carbonate. This value was approached faster on boiling of the solution, and slower upon standing at

room temperature.

Solubility of Calcium Fluoride and Tricalcium Phosphate.-The solubility of calcium fluoride and tricalcium phosphate was also determined in similar sodium carbonate solutions.

After boiling 0.100 g. of calcium fluoride with one gram of sodium carbonate for two hours in 200 ml. of water, 75 per cent of the total fluorine could be titrated with thorium nitrate.

Similarly, tricalcium phosphate is partly decomposed by sodium carbonate. A sample of 0.930 g. was boiled for two hours with two grams of sodium carbonate in 100 ml. of solution. Phosphorus precipitated in the filtrate amounted to 13 mg., that is, 14.3 per cent of the total phosphorus.

REACTIONS OF FLUOROAPATITE WITH A GASEOUS PHASE

The possibilities of fluoroapatite reactions with a gaseous phase and the formation of gaseous products in such reactions are discussed in this chapter. A number of standard free energy changes were calculated and are tabulated for reactions involving materials for which the thermodynamic data were available. The major sources for the thermodynamic values used throughout this chapter are listed in the bibliography (40, 43, 53, 56, 61).

First it was necessary to calculate the free energies of formation of fluoroapatite and hydroxyapatite.

Formation of Fluoroapatite and Hydroxyapatite

The values for the standard free energy of formation, and the standard heat of formation of fluoroapatite and hydroxyapatite have not yet been published by K. L. Elmore, et al., who have determined the heat capacities and the solubilities (15, 16a,b) of these two apatites.

The data, however, can be calculated from the available solubility constants according to the equations:

$$\Delta F^O(aq.) - \Delta F^O(c) = -RT \ln K_{s.p.} \quad (at \ 298.16^O K.)$$

$$\Delta F^O(c) = \Delta H^O_{apatite} - T(S^O_{apatite} - \sum S^O {}_{elements})$$

By utilizing the heat capacity data, the free energy functions of these two apatites can be formed and used up to $1500^O K$. For the sake

of simplicity, the numerical values for only four temperatures have
been tabulated.

TABLE 3

FREE ENERGIES OF FORMATION OF FLUOROAPATITE AND
HYDROXYAPATITE AT FOUR TEMPERATURES

	$-\Delta H^{o}$	$-\Delta F^{o}$ Per Gram - Formula Weight			
	298.16°K.	298.16°K.	500°K.	1000°K.	1500°K.
Fluoroapatite	3266.6	3083.4	2960.8	2646.9	2330.5
Hydroxyapatite	3212.4	3020.2	2891.4	2561.6	2232.1

The conventional standard states were used for the elements
except that the standard state for phosphorus was the metastable solid
white modification at 298.16°K., and gaseous P_4 at higher temperatures.

The standard free energy changes for the reaction

$$3 \, Ca_3(PO_4)_2 \; + \; CaF_2 \longrightarrow Ca_{10}F_2(PO_4)_6$$
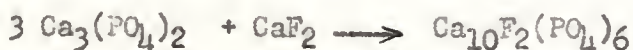
at the four temperatures are:-

ΔF^{o}(kcal.): - 9.6 (298.16°K.), - 9.2 (500°K.)

-10.5 (1000°K.),   - 4.0 (1500°K.)

The standard free energy values for the above reaction exhibit a
maximum which is probably due to the phase changes of calcium fluoride
and tricalcium phosphate near 1400°K.

The corresponding reaction for the formation of hydroxyapatite

$$3 \, Ca_3(PO_4)_2 + Ca(OH)_2 \longrightarrow Ca_{10}(OH)_2(PO_4)_6$$
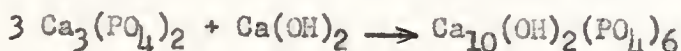
gives the following standard free energy changes:-

ΔF^{o}(kcal.): - 9.6 (298.16°K.), - 9.6 (500°K.)

-11.7 (1000°K.),   -19.3 (1500°K.)

For the higher temperatures it is assumed that Δ H of $Ca(OH)_2$ does not change and that the change in heat capacity of reactants and products is zero.

Reactions with Hydrogen-Containing Gases

The first group of reactants to be considered consisted of hydrogen-containing gases, and the reaction was assumed to produce gaseous hydrogen fluoride. The numerical values of the standard free energy changes of the following reactions designated by small letters, are presented for the four temperatures in Table 4.

The conversion of fluoroapatite into hydroxyapatite upon reaction with water vapor

(a) $Ca_{10}F_2(PO_4)_6 + 2 H_2O \longrightarrow Ca_{10}(OH)_2(PO_4)_6 + 2 HF$
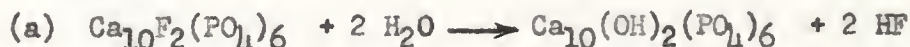
evidently does not proceed in the given temperature range, a conclusion which is supported by experimental evidence. The addition of acidic oxides would facilitate the decomposition of the original structure, for example, by using silica:

(b) $Ca_{10}F_2(PO_4)_6 + H_2O + SiO_2 \longrightarrow CaSiO_3 + 3 Ca_3(PO_4)_2 + 2 HF$

The actual decomposition of fluoroapatite with silica in the presence of water vapor takes place above $1500^{\circ}K$. The other oxides, the addition of which may exert similar beneficial effect are: Fe_2O_3, Al_2O_3, B_2O_3, TiO_2, etc.

The possible side reaction in the presence of silica (44):

$$4 HF + SiO_2 \longrightarrow 2 H_2O + SiF_4$$

has a positive standard free energy change at higher temperatures.

ΔF^O(kcal.): - 17.2 (298.16°K.), - 13.4 (500°K.)

- 2.7 (1000°K.), + 8.8 (1500°K.).

In the following examples not all the reaction products could be predicted with certainty. They were assigned arbitrarily for the purpose of providing an indication about the relative tendencies for various possible chemical reactions.

According to the arbitrary scheme

$$Ca_{10}F_2(PO_4)_6 + H_2Y \longrightarrow CaY + 3\ Ca_3(PO_4)_2 + 2\ HF$$

all the standard free energy values are positive for the hydrogen-containing gases, including HCl(c), HBr(d), H_2S(e), H_3N(f), etc. Y = two Cl, two Br, one S, two-thirds N.

The above scheme refers to the improbable condition that tricalcium phosphate remain intact. If it is assumed that it is rather calcium fluoride which remains among the products, the strongly acidic gases should decompose fluoroapatite at low temperatures.

The reaction with hydrogen chloride, for example, according to the following equation

(g) $Ca_{10}F_2(PO_4)_6 + 6\ HCl \longrightarrow CaF_2 + 3\ CaCl_2 + 6\ CaHPO_4$

has a negative standard free energy change at room temperature.

With hydrogen fluoride, the reaction should be far more energetic at the same temperature.

(h) $Ca_{10}F_2(PO_4)_6 + 6\ HF \longrightarrow 4\ CaF_2 + 6\ CaHPO_4$
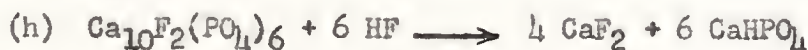
An excess of gas would probably further the reaction with the formation of monocalcium phosphate and more calcium halide. A large excess of the gas, however, should not readily yield the following products:

TABLE 4

STANDARD FREE ENERGY CHANGES OF REACTIONS OF
FLUOROAPATITE WITH A GASEOUS PHASE

Reaction	ΔF^o in Kilocalories Per Gram-Formula Weight of Fluoroapatite			
	298.16°K.	500°K.	1000°K.	1500°K.
a	+ 42.9	+ 43.7	+ 45.8	+ 44.7
b	+ 47.1	+ 40.2	+ 26.1	+ 5.3
c	+ 23.5	+ 22.2	+ 21.2	+ 9.8
d	+ 25.0	+ 24.1	+ 23.4	+ 12.5
e	+ 53.3	+ 46.7	+ 33.6	+ 13.3
f	+130.9	+121.5	+101.4	+ 73.9
g	- 4.6			
h	- 48.2			
i	+240.6	+312.5	+438.0	
j	+150			
k	-677.6	-631.7	-540.3	-459.4
l	-410.4	-425.3	-406.2	
m	-490.8	-380.5	-151.5	
n	-762.0			
o	-695.7	-604.3	-444.6	

(i) $Ca_{10}F_2(PO_4)_6 + 36\ HCl \longrightarrow 6\ POCl_3 + 9\ CaCl_2 +$

$$18\ H_2O + CaF_2$$

(j) $Ca_{10}F_2(PO_4)_6 + 36\ HF \longrightarrow 6\ POF_3 + 10\ CaF_2 + 18\ H_2O$
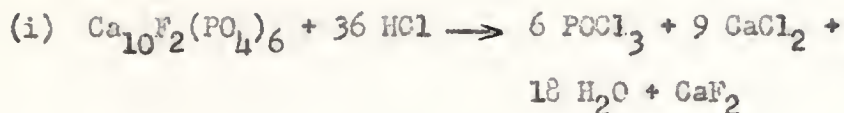
Experimental Tests with Gases

A number of tests were carried out in order to find experimental verification of the above-mentioned conclusions regarding the reactions with hydrogen-containing gases.

Several samples of finely ground (300 mesh) synthetic fluoro-apatite were subjected to the atmosphere of hydrogen and ammonia in the temperature range of 500° to $1000^\circ C$. for the duration of ten to twelve hours in an electrically heated tube furnace. Similar experiments were performed in the nitrogen atmosphere, which was saturated with water vapor at room temperature, with and without the presence of silica dust added to the sample.

Traces of fluorine-containing components could not be detected in any case in the exit gases which were passed through an alkaline solution.

The sensitivity of the test was about $8 \times 10^{-5} g.$ fluorine, i.e., 1 to 4000 of the total fluorine available in the sample.

Reduction of Fluoroapatite by a Gas Phase

The next group of reactions refers to the reduction of fluoro-apatite in contact with an active gas phase. The numerical values of the free energy changes are presented in Table 4.

Molecular hydrogen gives strongly positive standard free energy

changes in the given temperature range for the reaction

(k) $Ca_{10}F_2(PO_4)_6 + 15 H_2 \longrightarrow CaF_2 + 9 CaO + 5/4 P_4 + 15 H_2O$

Molecular chlorine is also ineffective[1] in the decomposition of pure fluoroapatite if the reaction is written as follows:

(l) $Ca_{10}F_2(PO_4)_6 + 18 Cl_2 \longrightarrow 6 POCl_3 + 9 CaCl_2 + 9 O_2 + CaF_2$

In contact with atomic chlorine (m), or hydrogen (n), the reduction yielding the same products as given above should occur readily.

An efficient low-temperature decomposition of fluoroapatite with a mixture of chlorine and carbon monoxide will probably take place according to the following scheme:

(o) $Ca_{10}F_2(PO_4)_6 + 18 CO + 18 Cl_2 \longrightarrow POCl_3 + 9 CaCl_2 +$
$18 CO_2 + CaF_2$
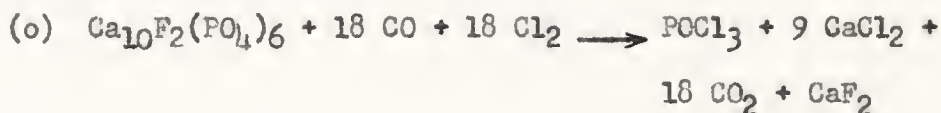
Conclusions

For the reaction of fluoroapatite with hydrogen-containing gases, it is improbable that hydrogen fluoride will be formed as a reaction product below $1000^\circ C$.

The decomposition of fluoroapatite structure may take place with strongly acidic gases at low temperatures, whereas fluorine remains in the solid phase, most probably as calcium fluoride.

The reduction of fluoroapatite without additives is not easy to effect under $1000^\circ C$., and takes rather drastic conditions as the use

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[1]It has been reported (11) that natural phosphatic nodules can be defluorinated in the presence of elementary chlorine at about 400° to $600^\circ C$. The volatile products are silicon tetrafluoride and phosphoryl chloride. In the presence of carbon and silica defluorination can be carried out at $500^\circ C$.

of atomic hydrogen, or chlorine.

In special cases a mixture of reactive gases, e.g., chlorine and carbon monoxide, might be efficient for a low temperature reduction.

REACTIONS IN THE SOLID STATE

Types of Solid State Reactions

Many types of solid state reactions of matter are known (10).

The simplest and most frequently occurring type is the additive reaction $A + B \longrightarrow AB$, where A and B may be elements or compounds. A large group of reactions in this category are the combinations of an acidic reactant with a reactant of basic nature to yield a salt. For example, $CaO + SiO_2 \longrightarrow CaSiO_3$.

The second mode of reaction between two solids is by exchange of constituents according to one of the following schemes:

(a) $A + BC \longrightarrow AC + B$ (b) $AB + CD \longrightarrow AD + BC$

(c) $ABX + CB \longrightarrow CBX + AB$
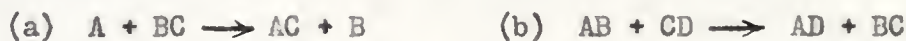
In these reactions which involve diffusion through two product layers, it is possible to have a considerable variety of phase arrangements determined by the miscibilities of product and reactant phases, and by the reaction mechanism.

Examples of reactions according to scheme (a) are found in the exchange of the metal of a salt for a more electropositive one.

Reactions conforming to scheme (b) are exemplified by the following: $CaO + NiCl_2 \longrightarrow CaCl_2 + NiO$; $CaO + PbCl_2 \longrightarrow CaCl + PbO$; or in combination with other reactions.

Reactions according to scheme (c) comprise a large group of

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reactions in which an oxygen-containing acid group is exchanged between one basic oxide and another: $MeO + Me'XO_n \longrightarrow Me'O + MeXO_n$.

The reaction temperatures in the last group, as in the others, show a correlation with the basic nature of the oxide involved; moreover, in contrast to the other types described, these reactions have in common the fact that the reaction temperatures for a given basic oxide are approximately constant and independent of the nature of the other reactant (carbonate, sulfate, phosphate, silicate).

The above principles were considered with a view to possible application on fluoroapatite by way of inducing permanent changes in the apatite lattice. In effect the application of these principles means that calcium should combine with acidic components other than fluoride and phosphate, for example, silicates and sulfates. In the presence of additional cations, e.g., sodium and magnesium, mixed salts and new phases could be formed.

Thermodynamic Considerations

Except for cases of miscibility of reactants and product phases, equilibrium is usually not possible in reactions in the solid state, and they proceed exothermally until at least one of the reactants is completely consumed. In practice, of course, complete reaction is difficult to achieve.

In a number of cases, the comparison of free energies of the reactants and of the products may give an indication about the tendency for a solid state reaction. Thermodynamic data were compiled for various groups of compounds over a range of temperatures for the purpose of free

energy calculations. Awareness, however, was maintained of the limita-
tions of such an approach because of incomplete data, and for other
reasons. For example, even if the free energy relationships should be
favorable, the thermodynamic requirements are by no means a safe cri-
terion for determining which phases actually will be formed in a
reacting system. Since the particle motion in solids is strongly
resisted and requires large energies of activation, unstable phases
might form and coexist with other phases for practically unlimited
times if the temperature is sufficiently low. Even when the reaction
products are the thermodynamically required phases, they may appear in
unstable states characterized by an excess energy content. Nevertheless,
the intention was only to establish a broad scale for various groups of
compounds in their relative readiness to react with fluoroapatite, inso-
far as there were proper data available. The results are summarized
in one of the following sections.

Apart from some preliminary tests, laboratory experimentation
was not carried out with regard to the solid state reactions for lack of
suitable analysis equipment and facilities for X-ray diffraction
photographs.

Studies of the solid state reactions could profitably be com-
bined with the determinations of diffusion and migration of the ions in
the fluoroapatite lattice as measured by the electric conductivity of
the crystal.

Exchange Reactions between a Pair of Salts

A large number of solid state reactions are known in which an

exchange of cations (or anions) takes place between a pair of salts at moderate temperatures with a measurable rate (10).

It is conceivable that the addition of some suitable salts to the apatite system might induce changes in the initial structure of the material whether by solid or liquid state reactions. It is possible that new phases would result which show increased solubility or enhanced susceptibility to the gas phase reactions. From this point of view, various possibilities were considered and many standard free energy changes were compared. The problem is essentially to find a salt, the anion of which would readily combine with calcium, and the cation of which would have a strong affinity toward fluoride or phosphate.

Among the most suitable compounds for the above-mentioned purposes are chlorides, sulfates, and sulfides; furthermore, silicates, borates, etc. First the tendency for fluoride exchange was considered in the simplified manner for calcium fluoride.

Chlorides.-The general reaction is:

$$CaF_2 + XCl_2 \longrightarrow CaCl_2 + XF_2$$

Of the nonvolatile chlorides, only beryllium and magnesium chloride exhibited negative standard free energy changes for the given reaction.

$BeCl_2$ — ΔF^o(kcal.): - 6.7 (298.16^{o}K.), - 16.6 (500°K.),
        -16.2 (1000°K.).

$MgCl_2$ — ΔF^o(kcal.): -12.3 (298.16^{o}K.), -13.5 (500°K.),
        -16.7 (1000°K.) , -16.9 (1500°K.).
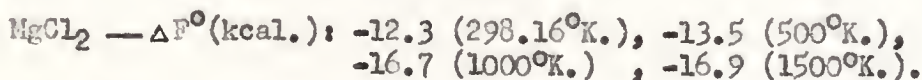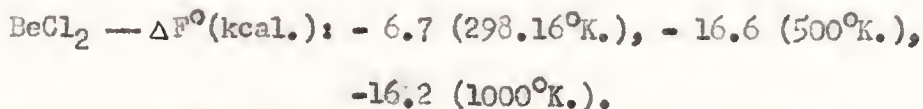
Other cations considered were: Li, Na, K, Sr, Ba, Fe, Pb, Cu, Co, Ni, Sn, and Al.

Herein must be included the possibility that the two gaseous chlorides, silicon tetrachloride and boron trichloride, might effect an exchange of fluoride for chloride in the solid phase, at least according to the standard free energy equations. The respective values are per one mole of calcium fluoride:

$SiCl_4$ —ΔF^o(kcal.): -10.1 (298.16°K.), -16.0 (500°K.).

BCl_3 —ΔF^o(kcal.): -15.1 (298.16°K.).
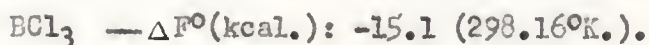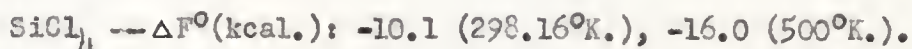
Sulfates.-The exchange of fluoride for sulfate between a pair of salts is generally unfavorable, except for magnesium sulfate. The cations considered were: Na, K, Mg, Zn, Pb, Fe, Mn, Cu, and Al. The free energy change for the reaction

$$CaF_2 + XSO_4 \longrightarrow CaSO_4 + XF_2$$

is positive in the order of 8 to 15 kcal. (for magnesium sulfate, it is negative by 2.2 kcal.) at room temperature per one mole of calcium fluoride, and 0 to 9 kcal. at 1000°K. The values decrease regularly with increasing temperature. Al[1], Fe and Cu offered the lowest positive free energy changes.

Sulfides.-For most sulfides the thermodynamic data for higher temperatures are deficient. At room temperature only Na, K, and Mg-sulfides exhibit negative standard free energy changes in the order of 4 to 6 kcal. for the reaction

$$CaF_2 + XS \longrightarrow XF_2 + CaS$$

The cations considered were: Na, K, Be, Mg, Ca, Ba, B, Al, Mn, Fe, Co, Ni, Cu, Zn, Sn, and Pb.

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[1]An aqueous solution of aluminum sulfate undergoes double decomposition with calcium fluoride (24).

Orthophosphates.-The meager data available on orthophosphates prohibited the extension of similar comparisons to the exchange of phosphate ion for other anions.[2]

Conclusion.-The possibilities for solid state reactions remain inconclusive until proper experimental testing, or until more thermodynamic data will become available.

Under actual experimental conditions, the formation of mixed salts, like CaClF and NaCaPO$_4$, and the existence of solid solutions must be considered, which further complicates the thermodynamic evaluation of possible solid state reactions.

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[2] It has been proved experimentally (26) that Sr and Ba replace Ca in phosphates (also in sulfates and silicates) in the solid state reactions between 500° and 600°C.

REACTIONS OF FLUOROAPATITE IN MELTS

A number of materials could be used as additives for high temperature reactions for the purpose of inducing changes in the fluoroapatite structure. The pure synthetic fluoroapatite has not yet been used for such experiments, but the fusion of phosphate rock with addition agents has been the object of many investigators.

Among the materials used there have been: furnace slag, alkali silicates, alkaline earth silicates, sodium carbonate, silica, alumina, magnesia, alkalies, magnesium silicates, magnesium sulfate, langbeinite, polyhalite, etc., and the mixtures of these. The individual references are listed in the following sources (7, 18b). The reaction temperatures are usually above $1000^{\circ}C.$, and no defluorination takes place.

Various experiments were carried out in this laboratory with synthetic fluoroapatite in salt melts.

Melts of Neutral Salts

The neutral salt melts can possibly induce partial replacements in the fluoroapatite lattice.

For example: one gram of fluoroapatite with five grams of sodium chloride kept in a platinum crucible for an hour at $900^{\circ}C$ yielded eight per cent of its total fluorine after leaching the product with water. A comparable amount of chlorine was found in the water-insoluble residue.

Melts of Basic Salts

The basic salt melts decompose fluoroapatite at high temperatures.

Fluoroapatite-sodium carbonate mixtures, with and without the presence of powdered silica, were heated to the maximum temperature of $925^{\circ}C$. in the course of six hours. The fusion products were leached with water, and the solutions were analyzed for phosphate. The extractions contained about one third to one fourth of the total phosphate in the sample. The value for released phosphate in the melts with silica was higher than in the melts without silica.

Fluoroapatite-sodium tetraborate mixtures at $1000^{\circ}C$. effected the decomposition of the starting material, and about ten per cent of the available fluorine was volatilized (possibly as boron trifluoride).

Melts of Acid Salts

The acidic melts should offer the best promise for the decomposition of fluoroapatite at medium temperatures.

First of all, metaphosphates may be considered because of their relatively strong acidity and convenient melting temperatures. The natural relationship of metaphosphates to the other phosphate systems would allow easier interpretation of the results, insofar as such systems have been observed in other studies. The high thermal stability and ease of preparation of metaphosphates speak in favor of their use.

In consideration of the above-mentioned advantages the latter part of this work will be devoted to the study of metaphosphate interactions with fluoroapatite, and other fluorine-containing materials.

INTERACTION OF SODIUM METAPHOSPHATE WITH FLUORIDES

Preliminary Observations

In the course of the studies about the reactions of fluorides in melts, it was observed that an interaction takes place between polyphosphate and fluoride ions with the formation of a phosphorus-fluorine containing gas (or gases), in addition to the evolution of hydrogen fluoride.

The initial system observed was calcium fluoride in sodium metaphosphate melt. Soon, however, it became evident that other fluorides, e.g., sodium and potassium behaved similarly.

A series of preliminary experiments was then carried out with calcium fluoride and sodium fluoride mixed with sodium metaphosphate and heated in dry nitrogen atmosphere for the purpose of determining the major factors affecting the rate and extent of the formation of volatile fluorine-containing gases.

The reaction started considerably below the melting point of any single component present, and was easily noticeable because of the immediate formation of white dense fumes as soon as the gas from the furnace came in contact with water or atmospheric moisture.

Literature Survey

The survey of literature revealed that the above-mentioned fluoride-metaphosphate systems have not been systematically studied,

except that the addition of fluorides to metaphosphates, usually in stoichiometric amounts, is the standard procedure for the production of the respective monofluorophosphates (29) which are known to decompose at higher temperatures with the reduction in the fluorine content of the salts (30). According to the information received from the Ozark-Mahoning Company concerning the fluorophosphate salts (73), neither the decomposition rates of these salts nor the reaction products have been investigated.

Tarbutton, et al. (65), let calcium fluoride react with phosphorus pentoxide at temperatures ranging from 500°C. to 1000°C., and identified phosphoryl trifluoride (POF_3) as the predominant volatile product of the reaction, along with some small amounts of phosphorus trifluoride (PF_3).

Gerard Montel (51) studied the same system, $CaF_2-P_2O_5$, over a wider range of compositions, and confirmed the results of the previous investigators.

These authors were primarily interested in the end products of the reaction and did not carry out studies of melts related to the rate of the formation of volatile fluorine compounds.

Objectives of Study of the Metaphosphate Melts

It was here attempted to determine systematically the major factors which affect the rate and extent of the evolution of volatile fluorine compounds from the metaphosphate melts containing fluorides.

The further intention was to determine whether the same relationships are valid for the decomposition of fluoroapatite in contact with

molten metaphosphate, and for the subsequent volatilization of fluorine-containing compounds.

The major variables were composition and temperature. The other factors considered were: duration of heating, presence of water vapor in the furnace atmosphere, size of charge, surface of the melt, rate of gas flow above the melt, pressure, type and mode of preparation of the used salts, particle size, and way of packing.

For the fluoroapatite tests the effect of added silica, sulfates, and sodium tetraborate to the metaphosphate melts was observed.

Use was made of three furnaces and experimental arrangements for obtaining the necessary data.

1. The vacuum furnace was constructed for the purpose of finding out the following information:

    a) whether it was possible to remove all of the bound water from the materials below the reaction temperature;

    b) the absolute pressure above the melt and the rate of gas evolution from the melt;

    c) the identity of the gases involved.

2. The tube furnace was used to measure the rate of gas evolution at constant temperature with varying composition and in controlled atmosphere. It was also used for heating the closed nickel tube which was attached to the vacuum system.

3. The crucible furnace served for the visual observation of the melts, and for the determination of the melting range of the mixtures. Also larger amounts of salts could be used for varying the depth of the charge.

The use of each method, and the actual experimental conditions are to be described separately in the following sections.

Selected Metaphosphate Systems

From among the numerous possibilities the following systems were chosen for a closer study. The reasons for the particular choices are indicated after each system.

1. $NaF-NaPO_3$ - Convenient temperature range. The single components have the following melting points: $NaPO_3$ $620^{\circ}C.$, NaF appr. $990^{\circ}C.$ Both salts are nonhygroscopic, provided that the meta-phosphate is in the form of crystalline tri-metaphosphate. Much is known about sodium metaphosphate melts as such in respect to the molecular weight distribution, density, surface tension, and viscosity (69).

2. CaF_2-NaPO_3 -The presence of two types of cations. and $NaF-Ca(PO_3)_2$ Effect of a bivalent cation replacing the monovalent cation. Relatively low reaction temperature, about 500° to $600^{\circ}C.$

3. Fluoroapatite-A special case of the previous system. $NaPO_3$ and The effect of crystal structure on the $NaPO_3-Ca_3$ $(PO_4)_2-CaF_2$ reactivity.

Some additional systems were also tested, e.g., calcium fluoride-calcium metaphosphate, sodium metaphosphate - various metal fluorides.

In preparing the materials for reaction, the mixing had to be

unifrom and the particle size defined. The standard sieves were used, 250 and 300 mesh, from the Newark Wire Cloth Company, Newark, New Jersey.

Characteristics of the Evolved Gases

General Observations.-The gas evolved from the melt strongly etched a silica tube and after passing through water, made it acidic. The presence of fluoride (or fluorosilicate) ions as well as phosphate ions could be proved in such a solution.

The solid adsorbents (soda lime, Ascarite, etc.) did not prove to be reliable for the total capture of the gases at a moderate flow rate, but a dilute alkaline solution cooled to ice temperature, was satisfactory for the absorption of the gas mixture for analysis.

The ratio of phosphorus to fluorine was relatively small in the analysis solution. Most of the fluorine was evidently evolved as hydrogen fluoride. Since the atmosphere above the melt was dry nitrogen, the hydrogen-containing component must have been provided by the ever-present chemically bound water in the melt.

The phosphorus-fluorine ratio in the trap was directly related to the amount of moisture present in the furnace. If the atmosphere above the melt was saturated with water vapor, the phosphorus content was very small, although sufficient for a qualitative proof, about 0.1 mg.

If the charge was heated gradually over a period of several hours, the P to F ratio became higher but not more than about one to seven, expressed in mole ratio. The gradual heating in the stream of dry nitrogen evidently removed some of the surface moisture of the constituent salts before the reaction started.

Separation of the Gaseous Phosphorus-Fluorine Containing

Component.-Attempts were made to find a suitable adsorbent which would

separate hydrogen fluoride from the rest of the gas mixture.

In one experiment, the gas from the furnace was passed through

a 3-cm. depth of phosphoric acid (85%, Reagent Grade) at the gas flow

rate of 80 ml. per minute. About seventy per cent of the total fluorine

had been absorbed but the P to F ratio still remained very low. Con-

centrated sulfuric acid used under the same conditions let more gas

through unabsorbed and the P to F ratio was approximately the same as

before.

Reagent Grade sodium fluoride powder was moistened and baked in

an oven at 110°C. for 24 hours. The dry aggregate was powdered to 250

mesh and filled into a narrow copper tube 100 cm. long. At a slow rate

of gas flow, 25 ml. per minute, all phosphorus and fluorine-containing

components of the gas mixture were adsorbed.

Next, the same narrow copper tube was filled with sodium fluoride

pellets and an increased gas flow rate was applied, 100 ml. per minute.

The source of the gas was 1.5 g. of calcium fluoride-sodium metaphosphate

mixture heated between 400° and 760°C. for three hours.

The analysis of the trap gave 1.0 milli-equivalents of fluorine

and 0.33 milli-equivalents of phosphorus. A duplicate confirmed the

result of a phosphorus-fluorine ratio one to three.

This proves that sodium fluoride pellets adsorb hydrogen

fluoride preferentially and at a moderate gas flow rate, a part of the

phosphorus-fluorine compound passes through the adsorbent.

There are three known phosphorus-fluorine containing gases[1]: POF_3, PF_3, PF_5; PO_2F is only assumed to exist (62).

Since it is highly improbable that the found P to F ratio results from a correct mixture of PF_5 and PO_2F, only the first two gases may be considered.

Phosphorus Trifluoride.-Phosphorus trifluoride (PF_3) is absorbed by aqueous bases producing fluorophosphate which reacts readily with potassium permanganate or bromine. Repeated attempts with these two reagents failed to yield evidence for a reduction-oxidation reaction, and therefore the only possible conclusion is that the major component of the phosphorus-fluorine containing gas is phosphoryl fluoride, even though the possibility of traces of other gases need not be denied.

Phosphoryl Trifluoride.-Phosphoryl trifluoride hydrolyzes (42) by steps according to the following scheme:

$$POF_3 \xrightarrow{H_2O} HPO_2F_2 \underset{HF}{\overset{H_2O}{\rightleftarrows}} H_2PO_3F \underset{HF}{\overset{H_2O}{\rightleftarrows}} H_3PO_4$$
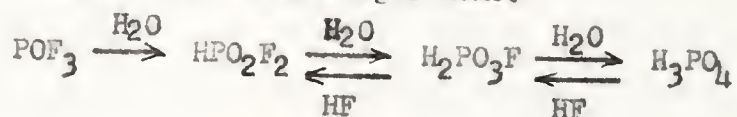
In an alkaline medium the respective salts which are readily soluble will be formed. Aqueous solutions of the alkali difluorophosphates react neutral but become acidic upon longer standing even at low temperatures. Heating accelerates the hydrolysis. The first products of decomposition are monofluorophosphates and they may be obtained in quantitative yields by boiling aqueous solutions of alkali difluorophosphates with very dilute solutions of the corresponding hydroxides.

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[1]excluding other elements, except oxygen, from the composition

The alkali monofluorophosphate solutions are neutral toward phenolphthalein but alkaline to methyl orange. Neutral or weakly alkaline solutions are not hydrolyzed on boiling for one hour. Heating in strongly alkaline solution results in rapid hydrolysis, and fast decomposition also occurs within a few minutes while heating in a strongly acidic solution.

As an example of phosphoryl trifluoride neutralization in dilute sodium hydroxide solution the following equation is presented:

$$POF_3 + 4\ NaOH \longrightarrow Na_2PO_3F + 2\ NaF + 2\ H_2O$$
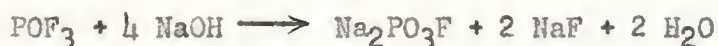
One molecule of phosphoryl trifluoride reacts with four equivalents of alkali. Phenolphthalein is used as an indicator. In acidic solution the hydrolysis would go one step further.

Difluorophosphoric Acid.-During the experiments with the tube furnace at lower temperatures, it was noticed that small droplets of a colorless liquid had condensed on the walls of the polyethylene tubing near the end of the nickel tube. These droplets were rinsed with small volumes of cool nitron[1] solution and thus removed from the tube. After standing for a few hours at ice-temperature, a slight colored precipitate was formed. The precipitates of several runs were combined, dried, weighed, and analyzed for fluorine. The weight ratio of fluorine to the whole sample (14.8 mg.) was about 1 to 10. The theoretical ratio for the compound nitron-difluorophosphoric acid (one molecule) is 10 to 109.

It may be assumed that the condensed material consisted primarily of difluorophosphoric acid[2] which is the first decomposition product of phosphoryl trifluoride with water.

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[1]Nitron is a shorter name for diphenyl-endo-anilo-hydro-triazole, which is an analytical reagent.

[2]The boiling point of difluorophosphoric acid (5) is appr. 110°C.

Construction of the Vacuum Furnaces

The Furnace for Crucibles.-A vacuum furnace was constructed which could accommodate a platinum crucible. Since the design was unique for a furnace of this size, the details of construction will be described.

Nichrome V resistance wire (B&S 24) was wound around a specially made nonporous porcelain core in a helix one-eighth inch in diameter and nine inches long (when closed). The total resistance was 20 ohms and the current was, for example, four amperes at $700^{\circ}C$. The dimensions of the core were: the diameter inside one inch, outside one and three-eighths inches, height two and three-quarters inches. The core was surrounded by two concentric radiation shields made of nickel sheet, one-one hundred twentieth inch thick. The diameter of the inner shield was two and one-quarter inches, of the outer shield two and eleven-sixteenths inches, the height three and three-quarters inches. The two shields were separated by porcelain spheres through which short pieces of nichrome wire held them together. There were also horizontal shields, two above and two underneath the core. The core and the shields were suspended by nichrome wire from three steel support rods eight inches high and one-eighth inch in diameter. Two of these wires served also for the conduction of current to the furnace. The support rods were screwed into the base which was a brass plate five-sixteenths inch thick. The connections through the base for the heating current as well as for the thermocouple wires, were made with the help of Stupakoff Kovar-Glass Terminals, Type FC, soldered through the plate.

The whole furnace was enclosed by a glass dome three and seven-eighths inches in diameter and ten inches high which rested in a groove in the brass plate. The dimensions of the grove were: outside diameter four and one-eighth inches, one-quarter inch wide, one-eighth inch deep. The vacuum seal between the plate and the glass was achieved by using the vacuum wax Apiezon W, which softens at about $80^{\circ}C$.

The platinum crucible rested in the middle of the furnace on a hollow porcelain rod through which the thermocouple junction was led up to the crucible without touching it. Through the center of the plate went a copper tube, three-eighths inch in diameter and fifty inches long which connected the furnace with the rest of the vacuum system. The furnace itself rested on a thermally insulated tripod which was firmly attached to the desk.

The furnace rendered good service at low pressures and reached high temperatures readily. The bottom plate did not become warmer than $45^{\circ}C.$, even when the furnace was at $800^{\circ}C.$ for several hours. The temperature control was affected noticeably by the pressure changes, and was not better than $\pm 5^{\circ}C.$ Baking of the furnace over a longer period of time at moderate temperatures did not remove the adsorbed gases completely and with an increase in temperature, slight degassing continued. Introduction of hydrogen into the system before opening it to the atmosphere improved subsequent evacuations.

According to the available data regarding phosphoryl trifluoride (65), it was not supposed to react with the furnace materials under the given conditions. Some etching of the porcelain core, however, became noticeable after the experiments, and silicon tetrafluoride was found to

be present in the liquid air trap. Since it was possible that the decomposition of the phosphorus-fluorine containing gas took place because of high temperature, and the presence of siliceous materials, another type of furnace was made use of for a number of experiments.

The Nickel-Tube Furnace.-An all-nickel tube (International Nickel Co., Mark:53965) was placed into a Hoskins electric tube furnace (Type FH 303 A, 15 V, 37 A) and connected to the copper tube leading to the vacuum system with Apiezon W wax. From the closed end of the nickel tube, a smaller tube of the same material, silver soldered to the larger one, led up to the middle of the furnace and housed the thermocouple. The dimensions of the tubes were as follows: larger tube had the length thirty-three and one-half inches, and the inside diameter fifteen-sixteenths inch; the smaller tube had the length nine and one-half inches, and the inside diameter three-quarters inch.

A Sorgel electric transformer (Type INS, sec. volts 17; 32.3 A) belonged to the tube furnace as an accessory.

The thermocouples were chromel-alumel junctions standardized against the melting points of pure inorganic salts, and compared to the other couples. The potentiometer used with the thermocouples was from Wheelco Instruments Co., Model 310.

The new apparatus had a smaller volume, 365 cc., as compared to 1600 cc. of the former. It also offered better degassing characteristics and closer temperature control. The disadvantage was that the size of the charge was limited by the capacity of the platinum boat. The platinum boat was placed into a larger zirconia boat so as to avoid the contact of platinum with the nickel tube.

This furnace operated in a satisfactory manner and an example of the measurements is presented in the next section.

Method of Measurement with the Vacuum Furnaces

When the furnace was below 300°C., a vacuum of the order of 10^{-3} mm. was reached in a couple of hours. At higher temperatures it took considerably longer, about a day.

The vacuum system on the rack consisted of a McLeod gauge, a mercury manometer, three traps, and provisions for removing material from the system. The one-stage mercury diffusion pump was backed by a Welch Duo-Seal vacuum pump. As a safety precaution, the water flowing through the cooling jacket of the diffusion pump operated a relay regulating the heating current of the diffusion pump, thus securing safe over-night operation of the pump without supervision.

The rate of the gas evolution was determined in the following manner:- While the system was open to the pumps, the pressure was measured with the McLeod gauge. Then the pumps were cut off by closing a stopcock and letting the system stand for five minutes (or some other known period of time), whereupon the pressure was again measured. The liquid air trap was opened simultaneously with the closing of the furnace. After 5 to 15 minutes, the pressure was determined again. The difference between the two last measurements made it possible to calculate the amount of condensible gases evolved from the melt in the given time period at a known temperature. After such a series of measurements, the system, including the furnace, was pumped empty through the other liquid air trap.

The volumes were: the McLeod gauge 282 cc., the rest of the glass system minus the traps 312 cc., a single trap 18 cc., and the furnace 365 cc.

Experimental Results of the Vacuum Measurements

The results showed that water was held very tenaciously by the melts, and that even prolonged heating (12 hours and longer) under reduced pressure (10^{-3} mm.) in the temperature range from 300°C. to 500°C., did not remove the hydrogen-containing constituent completely.

When the temperature was raised above 500°C., the reaction gradually started and gases condensible in the liquid air trap were present in the vacuum system.

The rate of gas evolution did not present any sharp maxima in its temperature dependence. It usually showed somewhat higher values immediately after the rise in temperature but then levelled off to a rate which decreased slowly at a given temperature.

For example, a charge of 5.0 grams of the standard sodium fluoride-sodium metaphosphate mixture with the platinum boat in the nickel tube was preheated under vacuum for twelve hours. With a gradual rise in temperature above 500°C., the following rates were observed:

TABLE 5

RATE OF GAS EVOLUTION FROM METAPHOSPHATE MELTS
IN THE VACUUM FURNACE

Temperature $^\circ$C. ± 5	Time Period Above 500°C. in Minutes	Rate Expressed in Moles of Gas per Minute $\times 10^5$ ± 0.1	Remarks
510	60	1.7	Steady Temp.
530	90	3.7	Steady Temp.
540	120	3.8	Steady Temp.
580	150	3.9	
594	160	5.6	Increased Temp.
628	270	5.0	Steady Temp.
630	300	5.0	Steady Temp.
713	380	11.2	Increased Temp.
716	480	3.9	Steady Temp.
790	560	5.6	Increased Temp.
800	630	2.8	Steady Temp.

These rates refer to the mixture of gases the pressure of which was measured in the system. The analysis showed that silicon tetrafluoride was the major component in the gas phase, with about ten per cent of a phosphorus-containing component.

Traces of hydrogen-containing compound (probably in the form of water) still present in the melt evidently interfere with the assumed formation of phosphoryl trifluoride, and produce hydrogen fluoride

instead which in turn attacks the siliceous parts of the apparatus with the formation of silicon tetrafluoride and water. This water may attach itself to phosphoryl trifluoride, causing the decomposition of the latter to difluorophosphoric acid and hydrogen fluoride.

Thus, even the smallest traces of water vapor may decompose most of the phosphoryl trifluoride, the total quantity of which is rather small to begin with in the order of about $7x10^{-3}$ moles of gas for the given charge of five grams.

In the above example, the trap contained $1.18x10^{-3}$ moles of gas. The analytical determination gave the following values: fluorine $4.6x10^{-3}$ equivalents, phosphorus $0.13x10^{-3}$ equivalents, and silica.

No etching was visible in the other parts of the glass apparatus except in or near the liquid air trap where most of the decomposition of the gaseous components seemed to have taken place.

The other experiments in the vacuum furnaces gave similar results.

Experimental Procedure at Atmospheric Pressure

Furnace.-The same tube furnace as described previously served for the series of experiments presented in the following text. First a Sillimanite tube, Coors Porcelain, was used, but since there was some contamination of the outcoming gas with silicon tetrafluoride, it was replaced with a nickel tube. The dimensions were: length twenty-five and one-half inches, inside diameter fifteen-sixteenths inch; to this another smaller nickel tube was attached: length fourteen inches, inside diameter one-half inch. A copper nipple was silver-soldered to the free

end of this tube. It was provided with threads for the adjustment of polyethylene tubing, twenty inches long, which led to the bottom of a one-liter polyethylene flask. Another tube through the cap led to the second trap. The other end of the larger nickel tube was closed with a hard rubber stopper through which passed a short piece of nickel tubing of a small diameter. On the furnace side of the stopper, asbestos tape was wrapped around the incoming end of the small nickel tube in order to protect the rubber from the heat radiation.

The temperature was measured with a protected chromel-alumel thermocouple in a porcelain sheath. After a steady temperature state was reached, the thermocouple was withdrawn for the duration of the experiment.

The furnace atmosphere was formed by Linde's dry nitrogen, which was passed through a four foot column of silica gel before entering the furnace.

Treatment of the Gaseous Reaction Products.-The outcoming reaction products diluted with nitrogen entered the polyethylene bottle which was immersed in ice water, and contained 50 to 75 ml. 0.1 normal sodium hydroxide solution. The absorption of the acidic components of the gas took place very readily, and only small amounts of it reached the next flask. The collection of the gas continued at least half an hour beyond the time of the removal of the boat from the furnace, since it was observed that some of the acidic components of the reaction products condensed or were adsorbed on the walls near the cooler outgoing end of the nickel tube. Heating this end with gas flame removed practically all the adsorbed materials, and an additional 5 to 15 per cent of the total

was usually recovered.

The sodium hydroxide solution in the traps was back-titrated with a dilute nitric acid solution, and the number of equivalents neutralized by the furnace gas was thus determined. All the solutions with condensed products were collected and analyzed for fluorine and phosphorus. Frequent blank runs were carried out between the experiments for checking purposes.

Standard Mixtures and Conditions

On the basis of the preliminary tests, a set of standard conditions was chosen and defined with which the effect of varied experimental factors could be compared.

Standard Conditions.-The standard conditions were as follows: A charge of 1.50 g. in a platinum boat was held in the hot zone of the furnace, at 700°C. (± 5°C.), for one hour while a stream of dry nitrogen swept the furnace at a rate of 110 to 130 ml. per minute. The platinum boat (length 7.5 cm., depth 1.0 cm.) was lying in a zirconia boat surrounded by a cylindrical sheath of thin nickel sheet, to which was attached a piece of nichrome wire for the centering and fast removal of the charge. The surface of the molten charge was about 6 sq. cm., and the depth about 3 to 5 mm.

Standard Compositions.-There were two standard compositions: one with sodium fluoride and the other with calcium fluoride. In terms of equivalents, the compositions were identical in respect to the fluoride and the metaphosphate content, viz., 18.9 mole per cent of fluoride and 31.1 mole per cent of metaphosphate, counting the anions and cations

separately in forming one hundred per cent. The original mixture, which was also used for the vacuum furnace experiments, had resulted from mixing one gram of sodium fluoride with four grams of sodium metaphosphate.

The materials were finely ground and intimately mixed. When the mixture was transferred into the platinum boat, the powder was not pressed in too tightly, only the top was smoothed with a spatula. The charge was dried for about thirty minutes with the boat in an oven at 150°C., and was then directly placed into the hot zone of the furnace.

Samples of Sodium Metaphosphate.-Three differently prepared samples of the same salt, Mallinckrodt's monosodium orthophosphate mono-hydrate, Analytical Reagent, were used for comparison. According to the mode of dehydration, the three preparations were designated as (a), (b), and (c) samples.

$NaPO_3$ (a)   Heated at 600°-620°C. for two hours; stored in a screw-capped bottle for four months.

$NaPO_3$ (b)   Heated gradually up to 800°C., let stand at this temperature for twelve hours, cooled slowly to about 600°C., held there for two hours. The salt was removed from the furnace at 400°C. and used immediately.

$NaPO_3$ (c)   Heated slowly in the course of three hours to 450°C. The product was used immediately.

Experimental Results of the Measurements at 700°C.
with the Standard Compositions

The purpose of the first series of experiments was to follow the effects of various factors, other than temperature and composition, on the reduction in the fluorine content of the samples, and to establish the limits of reproducibility of the data. Table 6 presents the results, expressed in terms of equivalents neutralized in the traps.

There is a marked difference in the values of sodium and calcium fluoride compositions, which runs consistently through all tests, the mixture with calcium fluoride always offering a higher yield. Since this difference is too large to be ascribed to the influence of varying moisture content, or the presence of impurities in the respective salts, it must result from a stronger effect of the calcium ion to further the reaction.

The mode of sodium metaphosphate preparation may also change the yield considerably. However, it is not so much the length of heating of the compound as the aging of the material which seems to play a role. Much, undoubtedly, depends upon the way of cooling of the product, since this determines the crystallinity and the hygroscopic properties of the resultant sodium metaphosphate.

The presence of water vapor in the atmosphere exerted benefical influence upon the reduction in the fluorine-content of the samples. Doubling of the reaction time did not improve the yield significantly; and the rate of gas flow seemed to be immaterial in the given range.

The reproducibility of the single runs ranged from two to four per cent deviation from the mean. Usually the accuracy was somewhat

better for the mixtures with the calcium component than with sodium.
All sodium metaphosphate melts showed spreading of the melt on the walls
of the boat, but with sodium fluoride-sodium metaphosphate mixtures the
tendency was particularly pronounced. Several erratic values, usually
coinciding with spilling or strong spreading of the melt, had to be
discarded.

The yield was not proportional to the size of the charge and
generally suffered a relative decrease when the charge increased.

Fluorine analysis in the trap solution gave usually a quite
close value to the number of equivalents neutralized by nitric acid,
although at times it was slightly lower. The two values could be con-
sidered practically equal after the correction for a blank was made.

The presence of the phosphorus-containing component was evident
in all runs, although the phosphorus-content in the trap was rather low,
seldom exceeding 0.2 milli-equivalents, and sometimes only sufficient
for a qualitative proof.

Variation in Composition at 700°C.

The next series of experiments dealt with the variation of com-
position of the melts. The results were expressed in percentages of
fluorine expelled from these melts. The total fluorine content of the
sample counted as one hundred per cent.

The previously used salts, sodium fluoride and calcium fluoride,
were mixed in varying proportions. In two cases calcium metaphosphate
replaced sodium metaphosphate. For comparison, use was made of a
commercial disodium monofluorophosphate salt.

TABLE 6

EFFECT OF EXPERIMENTAL CONDITIONS AT 700°C. ON THE EVOLUTION OF
FLUORINE-CONTAINING GASIS FROM METAPHOSPHATE MELTS

Composition of the Charge	Milli-equivalents Titrated in Traps		Special Conditions
NaF-NaPO$_3$ (a)		5.49	Standard
		5.70	Standard
		5.58	Standard
		5.74	Standard
	Mean	5.63 $\pm$ .14	
		6.71	Presence of water vapor
		4.31	One-gram charge
		4.24	One-gram charge
		7.01	Two-gram charge
		5.72	Double Gas Velocity
NaF-NaPO$_3$ (b)		4.02	Standard
		3.71	Standard
		3.96	Standard
	Mean	3.90 $\pm$ .15	
NaF-NaPO$_3$ (c)		4.05	Double time

TABLE 6--<u>Continued</u>

Composition of the Charge	Milli-equivalents Titrated in Traps		Special Conditions
CaF_2-$NaPO_3$ (a)		6.77	Standard
		6.62	Standard
		<u>6.57</u>	Standard
	Mean	6.65 $\pm$ .12	
		6.81	Double time
		4.39	One-gram charge
		7.58	Two-gram charge
CaF_2-$NaPO_3$ (b)		5.55	Standard
		5.33	Standard
		<u>5.39</u>	Standard
	Mean	5.42 $\pm$ .12	
CaF_2-$NaPO_3$ (c)		5.39	Standard

The sources for the used chemicals were:

NaF   Merck, Reagent Grade, dried at $110^{o}C$.

CaF_2 "Baker Analyzed", rinsed with water, ignited at 800°C. for an hour.

$NaPO_3$ Preparation (a), previously described.

$Ca(PO_3)_2$ Prepared from monocalcium phosphate monohydrate, Fisher Certified Reagent. Described previously.

Na_2PO_3F Ozark & Mahoning Company, dried at $110^{o}C$.

The tests were carried out under standard conditions as defined in the preceding section. At least duplicate samples were tested of each composition and Table 8 presents the mean values of the reduction in the fluorine-content of the samples.

The results revealed that an increasing PO_3 to F mole ratio furthered strongly the fluorine volatilization. The absolute quantity of the removed fluorine was smaller for the composition of the mole ratio 1 to 1, than either for a moderate excess of sodium fluoride or of sodium metaphosphate. The reason must be related to the salt formation at this mole ratio. The tendency for any reaction of the fluoride ions is lowered in such a case, since fluoride forms a part of the salt (Na_2PO_3F).

The ready-made compound, obtained from Ozark & Mahoning Co., gave a yield of volatile fluorine-containing compounds comparable to that of a salt mixture of equal composition. A somewhat higher value of the yield from the former may have been due to a different moisture content.

The difference in the behaviour of melts containing calcium and sodium, as observed before, persisted throughout the varying compositions.

TABLE 7

COMPOSITIONS OF THE EXPERIMENTAL METAPHOSPHATE-FLUORIDE MIXTURES

Per Cent in Equivalents of the Salt	Elements and PO_3 Component	Per Cent in Equivalents	Weight Per Cent	Milli-equivalents of Fluorine in a 1.5 g. sample
$NaF - NaPO_3$	Na	50.0	29.0	
	F	18.9	9.1	7.15
37.8 62.2	PO_3	31.1	61.9	
(standard)				
$CaF_2 - NaPO_3$	Na	31.1	18.3	
	Ca	18.9	9.6	
37.8 62.2	F	18.9	9.2	7.26
(standard)	PO_3	31.1	62.9	
$NaF - NaPO_3$	Na	50.0	35.6	
	F	31.1	18.3	14.43
62.2 37.8	PO_3	18.9	46.1	
$CaF_2 - NaPO_3$	Na	18.9	13.8	
	Ca	31.1	19.9	
62.2 37.8	F	31.1	18.8	14.85
	PO_3	18.9	47.5	
$NaF - NaPO_3$	Na	50.0	25.5	
	F	10.0	4.2	3.32
20.0 80.0	PO_3	40.0	70.3	
$CaF_2 - NaPO_3$	Na	40.0	20.6	
	Ca	10.0	4.5	
20.0 80.0	F	10.0	4.3	3.37
	PO_3	40.0	70.6	
$NaF - Ca(PO_3)_2$	Na	20.0	12.0	
	Ca	30.0	15.8	
40.0 60.0	F	20.0	10.0	7.90
	PO_3	30.0	62.2	

TABLE 7--<u>Continued</u>

Per Cent in Equivalents of the Salt	Elements and PO$_3$ Component	Per Cent in Equivalents	Weight Per Cent	Milli-equivalents of Fluorine in a 1.5 g. sample
CaF$_2$ - Ca(PO$_3$)$_2$	Ca	50.0	26.7	
	F	20.0	10.1	8.00
40.0 60.0	PO$_3$	30.0	63.2	
NaF - NaPO$_3$	Na	50.0	32.0	
	F	25.0	13.2	10.40
50.0 50.0	PO$_3$	25.0	54.8	
CaF$_2$ - NaPO$_3$	Na	25.0	16.3	
	Ca	25.0	14.2	
50.0 50.0	F	25.0	13.5	10.65

TABLE 8

EVOLUTION OF FLUORINE-CONTAINING GASES FROM METAPHOSPHATE MELTS
AT VARIOUS COMPOSITIONS

Composition Per Cent in Equivalents		Milli-equivalents Titrated $\pm$ 0.15	Milli-equivalents of Fluorine Present in a 1.5 g. Sample	Per Cent by Weight of Fluorine Removed $\pm$ 3 (average)
NaF - NaPO$_3$				
20.0	80.0	3.10	3.32	93.5
37.8	62.2	5.63	7.15	78.8
50.0	50.0	4.61	10.40	44.3
62.2	37.8	5.89	14.43	40.8
CaF$_2$ - NaPO$_3$				
20.0	80.0	3.25	3.37	96.5
37.8	62.2	6.65	7.26	92.2
50.0	50.0	5.78	10.65	54.2
62.2	37.8	7.00	14.85	47.2
NaF - Ca(PO$_3$)$_2$				
40.0	60.0	6.74	7.90	85.5
CaF$_2$ - Ca(PO$_3$)$_2$				
40.0	60.0	2.34	8.00	29.3
Na$_2$PO$_3$F		5.20	10.40	50.0

The stoichiometrically analogous mixtures made up from the salt pairs CaF_2-$NaPO_3$ and $Ca(PO_3)_2$-NaF gave rather close values in respect to the reduction in the fluorine-content of the samples. This is an indication that the effective composition of the melt is significant rather than the combination of initially added salts.

Even the calcium metaphosphate-calcium fluoride system lost part of its fluorine-content at this temperature, in spite of the high melting points of the individual components. In this case no melting had taken place; the powder was slightly sintered, however.

Temperature Dependence

The increase in temperature generally enhanced the reaction, and the fluorine-content of the samples was successively decreased under the conditions of the standard procedure.

Table 9 shows the respective mean values for the experiments with the standard mixtures of calcium and sodium fluoride with sodium metaphosphate. The melts with calcium fluoride exhibit higher yields in the fluorine-containing gases.

Reactions Involving Other Cations

Since the interaction between fluorides and metaphosphates was assumed to be a general reaction, it was considered interesting to let sodium metaphosphate react with fluorides other than sodium and calcium salts.

Some of the available materials were tried and samples were prepared which corresponded to the composition of the standard samples in respect to fluorine equivalents. The experimental conditions remained

TABLE 9

EVOLUTION OF FLUORINE-CONTAINING GASES FROM METAPHOSPHATE
MELTS AT VARIOUS TEMPERATURES

Composition	Percentage by Weight of Fluorine Removed		
	600°C.	700°C.	800°C.
NaF - NaPO$_3$ 37.8- 62.2%	62.8$\pm$5.0	78.8$\pm$3.0	85.5$\pm$3.0
CaF$_2$ -NaPO$_3$ 37.8 -62.2%	72.5$\pm$4.0	92.2$\pm$2.0	97.0$\pm$2.0

the same.

The sources for the other fluorides were:

KF   General Chemical Division, anhydrous.

BaF$_2$ "Baker's Analyzed", anhydrous.

AlF$_3$ A.D. Mackay, Inc.

ZrF$_4$ A.D. Mackay, Inc.

The accompanying chemical analysis of the fluorides gave the
stoichiometric fluoride values for anhydrous potassium fluoride and
barium fluoride. Aluminum fluoride and zirconium fluoride contained an
undetermined amount of moisture and less fluoride than expected from the
formula. Therefore, the titration data for the last two salts present
actually the minimum calculated percentage for fluoride removed from the
test samples. Potassium fluoride is a very hygroscopic salt, therefore,
the weighing and mixing of this salt was performed in a dry box and

closed containers. However, while transferring the mixed charge into the furnace, some atmospheric moisture may have been adsorbed by the salt.

TABLE 10

EVOLUTION OF FLUORINE-CONTAINING GASES FROM METAPHOSPHATE MELTS
IN THE PRESENCE OF OTHER CATIONS

Fluoride	Milli-equivalents Titrated (duplicates)		Fluorine Present in the Sample (calc.) mg.	Percentage by Weight of Fluorine Removed ±2.5
KF	5.94	5.62	135	93.0
BaF$_2$	4.19	4.36	105	77.2
AlF$_3$	3.82	3.78	126	53.5
ZrF$_4$	4.30	4.18	118	64.0
CaF$_2$	5.42 (mean)		138	92.2
NaF	3.90 (mean)		136	78.8

The extent of the reduction in the fluorine-content of the mentioned fluorides is comparable to that of sodium and calcium fluoride. The results are tabulated in the above table.

INTERACTION OF METAPHOSPHATE WITH FLUOROAPATITE

Experimental Conditions

As the preliminary tests had indicated, a destructive decomposition of fluoroapatite takes place when the material is in contact with sodium metaphosphate above $550^{o}C$.

An independent series of measurements was performed in order to establish the extent of fluorine removal from fluoroapatite under standard conditions. Subsequently, the variations in temperature and composition, the presence of moist atmosphere, and supplementary materials were imposed upon the system.

The standard composition in this case consisted of fifty per cent (by weight) of sodium metaphosphate (preparation c) with finely ground (300 mesh) fluoroapatite (preparation b).

All samples were tested at least twice, and the tabulated percentages present the respective mean values. Fluorine analysis was carried out in each case in the trap solution, as well as in the residue of the sample. No spreading of the melt occurred with these compositions, and the reaction product could easily be removed from the boat.

General Results

The results showed that a considerable proportion of fluorine was removed from the 1.5 g. charge within one hour at $700^{o}C$. Two other ratios of fluoroapatite to metaphosphate (see Table 11) were tested, but

TABLE 11

COMPOSITIONS OF METAPHOSPHATE MELTS
CONTAINING FLUOROAPATITE

Composition	Percentage by Weight of Fluorine Removed
50% fluoroap. - 50% $NaPO_3$	$56.9^{+}-2.0$
25% fluoroap. - 75% $NaPO_3$	$43.4^{\pm} 4.0$
75% fluoroap. - 25% $NaPO_3$	$33.4^{\pm} 4.0$
25% fluoroap. - 25% $Ca_3(PO_4)_2$ -50% $NaPO_3$	$53.5^{\pm} 4.0$
25% fluoroap. - 25% hydroxyap.-50% $NaPO_3$	$54.2^{\pm} 4.0$

in either case the yields were lower. The probable explanation is that with the smaller amount of sodium metaphosphate, the acidity of the melt is lower, and with the larger proportion of metaphosphate, the viscosity of the melt may exert a retarding influence on the rate of fluorine removal. The latter assumption was supported by the experiment in which tricalcium phosphate replaced 25 per cent of sodium metaphosphate and effected an improvement in the yield of fluorine-containing gases rather than a decrease.

The use of hydroxyapatite in place of tricalcium phosphate did not change the result. The amount of hydrogen which hydroxyapatite may contribute is small (about 0.3 mg.), compared with the rest of bound water. Hydroxyapatite was prepared according to the method of Rathje (57).

A mixture of calcium fluoride and tricalcium phosphate was made

up with sodium metaphosphate, which was analogous to the standard
fluoroapatite-sodium metaphosphate in respect to its stoichiometric
composition. The extent of defluorination in the first sample was
larger than for the fluoroapatite charge; the difference, however, was
rather small.

The relationships between the conditional factors and the extent
of defluorination in fluoroapatite melts were expected to be somewhat
different from the results of the fluoride group, primarily because of
the relatively low fluorine content (about 1.8 per cent by weight) of the
fluoroapatite charges. Besides, solid phases were always present in the
fluoroapatite mixtures, whereas previously a majority of the fluoride
melts had formed a homogeneous molten phase.

Temperature Dependence

The most interesting result appeared in the temperature variation
of the experiments, where a maximum reduction in the fluorine-content of
the samples was displayed at about $640^{\circ}C$. The reaction became noticeable
at about $550^{\circ}C$., and proceeded best just above the normal melting point
of sodium metaphosphate (approximately $620^{\circ}C$.). With rising temperature,
the extent of defluorination of the melt decreased until $800^{\circ}C$. was
reached. From there on the decrease in the fluorine-content of the
samples gained again gradually with increasing temperature. See Table 12.

Evidently there are two different processes involved regarding
the reduction in the fluorine-content of the melts. The first one is the
decomposition of fluoroapatite, and the gradual removal of the fluorine-
containing volatile products, e.g., phosphoryl trifluoride, from the

TABLE 12

EVOLUTION OF FLUORINE-CONTAINING GASES FROM METAPHOSPHATE MELTS
CONTAINING FLUOROAPATITE

Temperature °C. ±5	Percentage by Weight of Fluorine Removed			
	Standard Conditions	Water Vapor Present ± 3.0	Silica Present ± 5.0	CaF_2 and $Ca_3(PO_4)_2$ ±2.0
575	47.7 ± 5.0			
600	65.2 ± 4.0			
640	79.6 ± 2.0	80.7	72.9	82.0
700	56.9 ± 2.0	65.0	75.1	69.0
800	50.4 ± 2.0	57.2	64.9	65.6
900	59.2 ± 4.0			
1000	63.0 ± 5.0			

melt. This process is presumably favored by an increase in temperature.
The other reaction may be the interaction of hydrogen-containing com-
ponents (e.g. water) in the melt or at the surface of the melt with
fluorine-containing components, facilitating the formation and expulsion
of hydrogen fluoride. This effect must be proportional to the concen-
tration of hydrogen-containing components.

Upon fast insertion of the material into the hot zone of the furnace
at higher temperatures, part of the surface-adsorbed moisture may be
vaporized and removed before it can participate in the reaction in the
molten phase. Just above the melting point of sodium metaphosphate a

relatively larger amount of water may be trapped by the incipient melt.

This assumption is supported by the observation that the presence of water vapor in the atmosphere above the melt favors fluorine evolution as hydrogen fluoride. The effect of moisture probably consists in the acceleration of the process. For example, a charge treated for two hours in a dry atmosphere gave about the same yield of fluorine-containing gases as the charge which was held for one hour in a wet atmosphere.

The Effect of Supplementary Materials

Small supplements, 0.1 g. of silicic acid (containing 20 per cent water) added to 1.5 g. standard fluoroapatite charge, induced an improvement in the expulsion of fluorine-containing gases above 700°C. Below that temperature such an effect was not evident. Some of the silica was found in the trap after the reaction, consequently it had participated in the reaction and had been volatilized as silicon tetrafluoride.

The other added salts (0.2 g. to each standard sample), sodium sulfate and sodium tetraborate, did not further the defluorination of the melt but rather suppressed it somewhat. Calcium sulfate gave a better yield, possibly because of the presence of some residual water of constitution. The respective mean values were: sodium sulfate 53 per cent, sodium tetraborate 53 per cent, and calcium sulfate 72 per cent of the total fluorine content of the sample removed at 700°C.

The sources for chemicals were:

Na_2SO_4 Mallinckrodt's Analytical Reagent, anhydrous.

$CaSO_4.2 H_2O$ Coleman & Bell Co., C.P., dried slowly and ignited at 500°C.

$Na_2B_4O_7$ Borax, Baker's Analyzed, C.P., dried first at 150°C. and then at 300°C.

$SiO_2 \cdot xH_2O$ Mallinckrodt's Analytical Reagent.

EXPERIMENTS IN THE CRUCIBLE FURNACE

Solubility of Salts in Molten Sodium Metaphosphate

The furnace in operation was an electric multiple unit crucible furnace from Hevy Duty Electric Co. (Type 82, 115V, 725W). Platinum crucibles were used in all experiments.

First the solubility of various salts in sodium meta phosphate melt was tested.

Small amounts of calcium fluoride disappeared in the melt quite rapidly at the beginning; later on, the process became slower, and after seven hours at 700°-850°C., about 2.5 g. of the salt had dissolved in 7.5 g. of sodium metaphosphate.

Tricalcium phosphate displayed a similar behavior in the same temperature range. In the course of six hours about twenty per cent by weight had dissolved in the melt.

Sodium fluoride was very readily soluble so long as there was not any excess of sodium fluoride. At the mole ratio 1 to 1, the melt gradually disappeared and crystalline salts were formed.

Fluoroapatite was very slow in becoming a homogeneous part of the melt. Possibly other solid phases of phosphates replaced the original structure since the decomposition of the material took undoubtedly place.

For example, in a mixture of 1.23 g. of fluoroapatite and 6.13 g.

sodium metaphosphate held for two hours at 850°C., the molten part was analyzed separately from the crystalline phase. The glassy part of the melt contained more than half of the total fluorine and about thirteen per cent of it had been volatilized. In this experiment, fluoroapatite powder was laid at the bottom of the crucible, and the decomposition products had to diffuse through a layer of 12 mm. of viscous melt before reaching the surface.

In another experiment in which the layer was even deeper, less than ten per cent of the total fluorine had been volatilized in the same period of time.

If a similar melt was held overnight for sixteen hours at about 800°C., half of the total fluorine still remained in the melt.

Analogous experiments with small amounts of sodium or calcium fluoride gave better yields of volatilized fluorine, the percentage of which was still considerably lower than in the case of tube furnace experiments.

Weight Loss of Standard Mixtures and the Component Salts

The rate of weight loss for various samples was determined in another series of experiments.

The standard compositions of sodium and calcium fluoride with sodium metaphosphate at 700°C. gave closely similar results. The total weight loss for a 1.5 g. charge was about 120 mg.

The highest weight loss, about one fourth of the total, occurred during the first quarter of an hour. In the last quarter, the rate was down to about four per cent of the total. During the first hour only

half of the total weight loss had taken place. From then on there continued a rather steady rate of weight loss for further twelve hours, decreasing gradually.

Additional tests confirmed the observation that after the first hour, the weight loss for a given sample had reached a slow steady state for a number of hours.

The weight loss of the standard charges upon drying in the oven at 150°C. for two hours was small, 1.1 to 1.4 mg. per 1.5 g. charge.

The ignited calcium fluoride, which was used in making up the mixtures, lost 0.45 per cent of its weight in 20 hours at 600°-700°C. The respective loss for sodium fluoride was 0.39 per cent in 15 hours at 600°-800°C.

A charge of 1.2 g. of sodium metaphosphate held in the tube furnace at 750°C. for two hours lost 0.1 mg. of its weight.

Microscopic Observations

Some of the crystalline phases which separated during the course of reaction, or upon cooling of the above-mentioned melts, were subjected to study under a petrographic microscope.

An excess of metaphosphate forms a glass when chilled rapidly, and on occasions the crystalline parts of a melt could be observed embedded in the optically isotropic glass, thus obviating the need to separate the crystals from the rest of the melt.
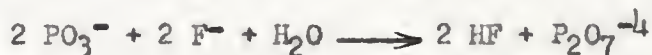
A variety of phases were observed, the type of which depended primarily on the composition of the melt and the rate of cooling. For example, in the system calcium fluoride-sodium metaphosphate the presence of calcium pyrophosphate was positively proved.

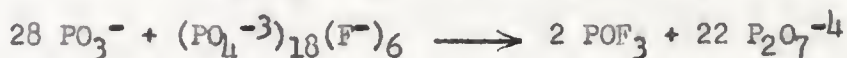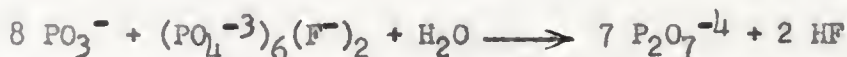# SUMMARY OF THE EXPERIMENTAL RESULTS WITH METAPHOSPHATE MELTS

Reaction Formulas

In all cases when sodium metaphosphate comes into contact with fluorides or fluoroapatite, above the temperature of about 550°C., reactions take place which liberate a considerable part of fluorine in the form of volatile compounds. Most of this fluorine is in the form of hydrogen fluoride. The hydrogen component is provided by the melt which always maintains small amounts of water, even though the constituent salts were dried and heat-treated before mixing. Evidence also points to the presence of phosphoryl trifluoride in the exit gas.

The basic reactions for fluoride are assumed to be:

$$2 \text{ PO}_3^- + 2 \text{ F}^- + \text{H}_2\text{O} \longrightarrow 2 \text{ HF} + \text{P}_2\text{O}_7^{-4}$$

$$5 \text{ PO}_3^- + 3 \text{ F}^- \longrightarrow \text{POF}_3 + 2 \text{ P}_2\text{O}_7^{-4}$$

The same reactions for fluoroapatite give the following equations:

$$8 \text{ PO}_3^- + (\text{PO}_4^{-3})_6(\text{F}^-)_2 + \text{H}_2\text{O} \longrightarrow 7 \text{ P}_2\text{O}_7^{-4} + 2 \text{ HF}$$

$$28 \text{ PO}_3^- + (\text{PO}_4^{-3})_{18}(\text{F}^-)_6 \longrightarrow 2 \text{ POF}_3 + 22 \text{ P}_2\text{O}_7^{-4}$$

In the case of the standard fluoroapatite-metaphosphate mixture (50 to 50%) at least five per cent of the material must have remained in the form of orthophosphate.

The Major Factors and Their Influence Upon the Reactions

The major factors which influence the extent of the reduction in the fluorine content are composition and temperature. The rate of

defluorination of the melt is markedly affected by the depth of the layer through which the decomposition products have to diffuse and by the presence of hydrogen-containing compounds as constituents of the melt.

For a given temperature the percentage of removed fluorine increases as the acidity of the melt increases. Herein the relative acidity of a metaphosphate melt (in respect to fluoride ion) is defined by the concentration of P-O-P bonds as they occur in polyphosphates (straight chains), and polymetaphosphates (cyclic structures). There is a rather abrupt increase in the percentage of removed fluorine as soon as the mole ratio of metaphosphate to fluoride exceeds one to one.

The rate of formation of fluorine-containing gases is highest immediately after a mixture has reached the reaction temperature. After the first hour the rate has slowed considerably, and under favorable conditions more than ninety per cent of the original fluoride in the sample has been volatilized.

Complete removal of the fluoride component of the melts was reached in no case with the standard compositions, not even at high temperatures (1000°C.) or with prolonged heating (12 hours and longer) under reduced pressure.

A large excess of metaphosphate, particularly if it formed a deep layer, impaired strongly the rate of expulsion of fluorine-containing gases. This effect must be due to the fact that the viscous melt impedes the transfer of the reaction products. This assumption was also supported by the observation that the total amount of fluorine removed was not directly proportional to the size of the charge, but decreased as the charge increased.

A rise in temperature generally favored the rate and extent of defluorination. Special conditions prevailed at low concentrations of fluorine in the presence of solid phosphate phases, as in the case of fluoroapatite melts. A maximum was exhibited in the formation of fluorine-containing gases just above the normal melting point of sodium metaphosphate (about 620°C).

The presence of water vapor in the furnace atmosphere was efficacious in promoting the evolution of hydrogen fluoride, but what seemed to be more significant was the concentration of the hydrogen constituent in the melt.

There was a consistent and marked difference in the yield between the melts containing sodium and calcium ions. Such a variation emphasizes the effect which different cations may have on the reaction, or for example, in respect to the viscosity of the melt.

The decomposition of fluoroapatite by metaphosphate was almost complete, judging from the comparison between the standard samples of fluoroapatite and the respective mixtures of calcium fluoride and tricalcium phosphate.

Small supplements of silica enhanced the defluorination by the formation of silicon tetrafluoride; the addition of calcium sulfate gave only slightly better results than the standard mixture, whereas sodium sulfate and tetraborate did not have any beneficial effect under the given conditions.

PHYSICAL INTERPRETATIONS

Metaphosphate Melts

The reactions of fluoride ions in salt melts at high temperatures
can be interpreted in the light of acid-base theory extended to non-
aqueous systems. From the point of view of the Lewis theory, the fluoride
ion acts as a strong base capable of reacting with high temperature acids,
which can be coordinatively unsaturated molecules like silica, or ions
such as metaphosphate.

Ions with medium ionic potential (B, Si, P) preferably tend to
form structures with oxygen bridges, thus building up macromolecules which
react as acids at higher temperatures. These so-called polyacids are
characterized by the linking of the single groups to large complexes by
means of oxygen bridges of the type X-O-X. The transition of a polyacid
to its corresponding base consists in breaking of an oxygen bridge, and
a simultaneous binding of an oxygen atom. The acid-base reaction is thus
connected with a disintegration of the macromolecular structure, as for
example, in the case of metaphosphates and silicates.

These macromolecules are built up of a network of PO_4 and SiO_4
tetrahedra, in the interstices of which are interspersed cations, such as
sodium or calcium. In the melt there is a certain degree of freedom of
motion for the individual cation, or tetrahedron, and undoubtedly there
exists a dynamic equilibrium while a continuous rearrangement and inter-
change of tetrahedra takes place (69). The occurrence of single

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phosphate ions in metaphosphate melts is rather improbable.

Effect of the Type of Cations

A distinct relationship exists between the acidity of the poly-acids and the cations present. Flood and Forland (20) working with pyrosulfates, concluded that the stability of the oxygen bridge S-O-S is greatly influenced by the polarizing power of the cation. The size of the cation is the decisive factor for the number of oxygen bridges broken per cation, provided that the polarizing power of the cation exceeds a certain amount.

A similar set of relationships may be expected to exist also in the metaphosphate melts which would explain the difference between the effect of sodium and calcium ions. The ionic radii of these ions are relatively close (Na=0.98; Ca=1.06), but since the polarizing power of calcium ion is larger owing to its double charge, the ease of breaking the P-O-P bonds should be enhanced by calcium ions. Barium ion should not be as effective as calcium ion because of its larger size and decreased power of polarization. Such a difference was observed experimentally. Because of the presence of moisture and uncertain chemical composition, the tests with other cations were not reliable enough to enable an extension of such conclusions to a variety of systems.

The problems regarding the effect of an individual cation on the volatilization of fluorine-containing compounds, as related to its size and charge, from salt melts, would form a special study which would necessitate the use of refined experimental methods and a complete exclusion of moisture from the starting materials.

Extension of the Reaction Concept

Besides cations, also anions other than metaphosphates could be considered in systems which would exhibit similar phenomena of anion-fluoride interaction in an acidic melt with the formation of volatile fluorine-containing compounds. Borates and silicates evidently form such systems. Furthermore, pyrosulfates form fluorosulfonates with fluorides, and it is known that fluorosulfonates decompose with the formation of sulfuryl difluoride (66).

Possibly even bichromates and metavanadates could behave similarly; they might, for example, form the products chromyl fluoride (CrO_2F_2), and vanadyl trifluoride (VOF_3).

The interesting subject - the possibilities and conditions of formation of volatile covalent fluorine compounds in salt melts - has not been previously treated from a general point of view, most probably because of lack of experimental data. It certainly would offer a new rewarding field of experimentation, and possibly contribute to the theory of the properties of salt melts.

CONCLUSION

The study of the various factors affecting the stability and inertness of fluoroapatite toward chemical reactions as compared with related materials, as well as with the component salts, should reveal interesting relationships between structure and reactivity which may prove to be meaningful in a wider context.

A significant feature of the fluoroapatite structure lies in the fact that it is chemically more resistant than either one of its component salts, calcium fluoride and tricalcium phosphate, or other minerals of similar structure. Since the physical and chemical properties of fluoroapatite are determined by the structure as well as by the size and properties of the component ions, further detailed studies of these physically determined facts may be profitable.

Recent developments in the investigation of phosphatic materials have provided reliable methods for the synthesis of reproducible fluoroapatite. Thus it has become possible to study the chemical reactivity of this material in its pure form. With the simplified method of fluoroapatite synthesis as described in this work, sufficient quantities of it can be prepared in reasonable time. The quality control of the product may be carried out by chemical analysis and microscopic observations.

The experiments in this laboratory confirmed the fact that pure fluoroapatite is a very stable substance and chemically quite inert

toward most chemicals even at elevated temperatures. The general possibilities of fluoroapatite reactions with chemicals in various phases were studied, and the following conclusions were reached for each phase.

The consideration of gas-solid reactions does not give much promise for the formation of volatile fluorine-containing compounds among the products below $1000^{\circ}C$. The destruction of the fluoroapatite structure, however, should be possible at relatively low temperatures in the atmosphere of highly acidic gases or mixtures of strong reducing agents. The addition of suitable solid reactants, for example, silica and carbon would facilitate the rate of such reactions with a gaseous phase.

According to the available thermodynamic data, there are few indications for solid-solid reactions below $1000^{\circ}C$. for the modification of the fluoroapatite structure with ordinary salts, but the possibility of special effects by the added materials is by no means excluded.

The melts should offer the widest variety of reactions with fluoroapatite. The neutral salt melts can possibly induce partial replacements in the fluoroapatite lattice. The basic salts react with fluoroapatite at higher temperatures and the acidic melts do the same in a lower temperature range.

Suitable combinations of two or three types of reactions as indicated above may give rise to fluoroapatite reactions proceeding at a rapid rate in the range of moderate temperatures. Such systems, however, will become too complicated for the deduction of new facts regarding the characteristics of the pure fluoroapatite structure.

The interaction of sodium metaphosphate with fluorides and fluoroapatite was studied in greater detail and a number of factors

influencing the reactions were considered. The major variables were composition and temperature. In all cases when sodium metaphosphate comes into contact with fluorides or fluoroapatite above the temperature of about $550^{\circ}C.$, reactions take place which liberate a considerable part of fluorine in the form of volatile compounds, mostly as hydrogen fluoride.

A special contribution of this work lies in the experimental proof that at least one gas containing phosphorus and fluorine, is released from the melt. Evidence points to phosphoryl trifluoride (POF_3) as a component among the gaseous products of the reaction. The relative amount of hydrogen fluoride as compared to phosphoryl trifluoride depends on the concentration of combined hydrogen in the melt and water vapor in the atmosphere above the melt.

The interaction of metaphosphate melts with fluorides is a general reaction independent of the type of fluoride and produces the same major products in the gaseous phase. There are indications, however, that the type of cation influences the rate of the reaction. For example, calcium ions seem to be generally more effective in furthering the gas evolution from the melt than the sodium ions.

The fluoroapatite structure is destroyed by sodium metaphosphate above $550^{\circ}C.$, and under favorable conditions the fluorine content of the sample is reduced by eighty per cent within an hour. The yield in the fluorine-containing gases shows a maximum at about $640^{\circ}C.$ The effect of various added materials (e.g. silica) upon the reaction was determined.

The results have been interpreted in the light of the acid-base theory according to the Lewis concept, and the possibilities for further extension of such studies have been indicated.

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BIOGRAPHICAL NOTE

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